LECTURES ON

THERMODYNAMICS

INTRODUCTION:
THE PRINCIPLES OF THERMODYNAMICS

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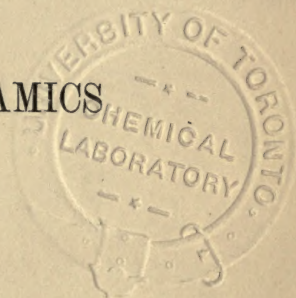
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THE INTRODUCTION OF A COURSE OF

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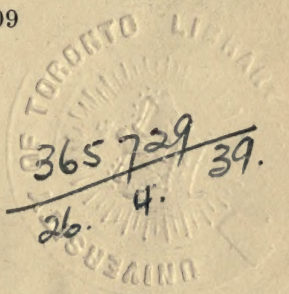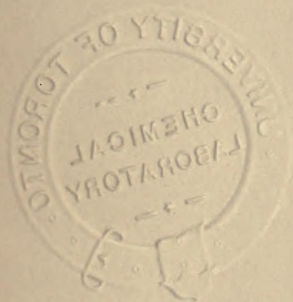
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THERMODYNAMICS

BOOK I. THE PRINCIPLES OF THERMODYNAMICS : PRINCIPLES OF THE THERMODYNAMICS OF BODIES SUBJECT TO ANY MECHANICAL FORCES

CHAPTER I. THERMODYNAMIC CHANGES OF STATE

1. Thermometry

One of the most fundamental concepts employed in the study of physical phenomena is the concept of the **temperature*** of a body. We distinguish, through touch, between 'hot' and 'cold' bodies. A block of ice feels 'cold'; the air in the evening feels 'cool'; a cup of tea feels 'lukewarm'; we boil it, and it feels 'hot.' We thus establish a qualitative scale of the degrees of hotness or 'temperatures' of bodies.

Any measurable physical property of a body, that is a continuous, uniform, and increasing (or decreasing) function of the degree of hotness of the body, is a **thermometric property** of the body. By serially numbering successive values of a thermometric property of a given body — of a 'thermometer,'— an arbitrary quantitative scale of the temperatures of the body is obtained. For each temperature is thus associated with a definite number. This renders it possible to bring the body at any time to any accessible assigned temperature. Instances of thermometric properties are the length of the thread of mercury in the capillary tube of an ordinary mercury-in-glass thermometer, the electrical resistance of a strip of metal, and the pressure of a mass of gas enclosed in a receptacle of constant volume. With reference to the arbitrary scale of any given thermometer, the temperature, when uniform, of any body can be determined by allowing temperature equilibrium to become established between the body and the thermometer; since it is observed that contiguous bodies having different temperatures come spontaneously to a common temperature.

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* For a most interesting and penetrating historical and critical discussion of thermometry, see Mach, Wärmelehre, pp. 3–77. Leipzig, 1896.

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A scale of temperatures established by arbitrary graduation of a given thermometric *instrument* cannot be reproduced in the absence of the instrument. A reproducible scale is obtained if the temperature is defined by any uniform, analytic, and increasing (or decreasing) function of a chosen thermometric property of some *substance*, i. e. if it is defined by any convenient relation connecting the temperature with the chosen property. The scale of temperatures of the ' constant pressure gas-thermometer ' is such a scale. This scale is suggested by an experimental observation made by Gay-Lussac, and is established in the following way.

Gay-Lussac observed that, when any given mass of any one of the more permanent gases is brought from any given temperature to any other given temperature, under *any* relatively low constant pressure, the mass expands very nearly the same fraction of its initial volume. More briefly, the *relative thermal expansion*

$$\frac{v_2 - v_1}{v_1}$$

of the gas is very nearly independent of the pressure. In particular, the expansion between the freezing and boiling temperatures, τ_0 and τ_{100}, of water is a little over one-third the volume at the lower temperature ; or, more exactly,

$$\frac{v_{100} - v_0}{v_0} = 0.366.$$

If we elect to measure differences of temperature,

$$\tau - \tau_0,$$

by setting them proportional to the corresponding relative expansions, we shall obtain a readily reproducible measure of temperature differences. And, in so far as the law of Gay-Lussac is true, this measure will be independent of the specific properties of the thermometric gas. We shall thus have

$$k(\tau - \tau_0) = \frac{v - v_0}{v_0} ;$$

and the numerical value of the temperature of reference τ_0 will remain arbitrary. In this formulation, the proportionality factor k is the relative expansion of the gas per degree of the proposed scale of temperature differences.

If the unit difference of temperature be determined by putting

$$\tau_{100} - \tau_0 = 100,$$

the value of k will be determined by

$$k(\tau_{100} - \tau_0) = \frac{v_{100} - v_0}{v_0}$$

$$k.100 = 0.366$$

$$k = 0.00366$$

$$= \tfrac{1}{273}.$$

Hereupon, the general equation

$$k(\tau - \tau_0) = \frac{v - v_0}{v_0}$$

becomes

$$\frac{\tau - \tau_0}{273} = \frac{v - v_0}{v_0};$$

which equation expresses the proposed measure of *changes* of temperature by means of thermal expansions.

The scale of temperatures is now most simply determined if we arbitrarily set

$$\tau_0 = 273.$$

For this reduces the general equation to

$$\frac{\tau}{\tau_0} = \frac{v}{v_0};$$

whereupon the general temperature is defined by the relation

$$\tau = \frac{273}{v_0} v;$$

it is, by definition, proportional to the volume of the mass of thermometric gas.*

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* It is important to understand that this definition of the function τ is perfectly arbitrary. It can be replaced by any other uniform, analytic, increasing function of the thermometric property v. The definition given is naturally arrived at in the manner indicated ; and it has a particular interest because of the fact that it is in common use.

Since equal volume-increments of the gas expanding under a constant pressure determine equal increments of the temperature τ, it appears that changes of temperature on this scale are measured by the quantities of *work* developed by the ex-
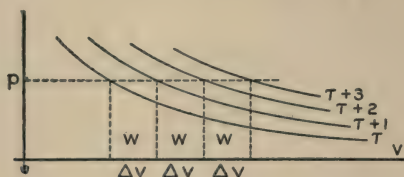
FIG. 1.

panding gas. The definition of the scale establishes a sort of work-measure of differences of temperature.

In the following pages, unless otherwise specified, the letter τ shall be understood to denote temperatures with regard to any thermometric scale that may be arbitrarily chosen.

When two blocks of metal having different temperatures are separated by a sheet of brass, the three bodies rapidly attain a common temperature; when the separation is effected by a sheet of asbestos the common temperature is attained far less rapidly. This is expressed by saying that the asbestos is 'thermally conducting' in a less degree than is the brass. The form of statement implies that the temperature equalization occurs *as if* the temperature of each participating body were determined by the amount of a fluid contained by it, this fluid flowing through the separating sheet from the hot body to the cold one. Bodies, then, are thermally conducting in different degrees. In the following, by a 'thermally conducting' body shall be meant a body permitting a rapid equalization of the temperatures of bodies contiguous with it; by a 'thermally non-conducting' body shall be meant a body permitting only a very slow equalization of these temperatures.

2. Physical changes of state

Physical science is concerned with 'physical phenomena,' with the mechanical, optical, thermal, electric, magnetic, chemical, properties of bodies and the changes that these properties are observed to undergo. An ensemble of changes of the physical properties of an assemblage of bodies is a 'physical process.' For convenience of study, physical processes may

be classified in accordance with the degree in which the physical character of the participating bodies is modified.

Thus, when a block of ice whose temperature is below the melting temperature of the substance is set in motion, the physical state of the block is changed very little. Only its position and velocity are altered. The body undergoes a *mechanical* change of state.

If the temperature of the block is raised, the ensuing alteration of the temperature and density of the body constitute a deeper-seated change of its physical state. The body undergoes a *thermal* change of state.

If the block is melted, and the resulting liquid is evaporated, the physical state of the body is yet more profoundly modified. The new state resembles the initial state very little. Yet the body is still regarded as being a mass of the same 'substance,' water; it has undergone changes of its *state of aggregation.*

If the block, finally, is converted into a mixture of hydrogen and oxygen gases, its physical properties are altered very deeply indeed. It is no longer regarded as being the same 'substance.' Its physical character is changed in almost every respect save in that of its mass. The body has undergone a *chemical* change of state.

3. Mechanical processes

Changes of the velocities and states of strain of bodies are termed mechanical processes. Of all changes of the physical states of bodies, the mechanical processes are among the most strikingly obvious, and are the least deep-seated. Because of their relatively simple character, comprehension of the way in which mechanical processes occur has been attained earlier and more comprehensively than has been the case in the study of any other class of changes of the physical states of bodies. At all times since the earliest recognition of mechanical laws, mechanics has been the highest developed branch of physical science.

Quantitative description of mechanical processes employs the principle of the conservation of mechanical energy. The mechanical work requisite to establish a state of strain of a body is stored as the 'potential energy' of the body. The work requisite to impart a given velocity to a body is stored as the 'kinetic energy' of the body. And in any purely mechanical process the sum of the potential and kinetic energies of the

participating bodies remains constant. The process may be, for example, the swinging of a pendulum in a vacuum, the movements of a mechanism driven by a falling weight, or the motions of the bodies constituting the solar system. In any case, the total mechanical energy of all the bodies participating in the process remains constant.

4. Supplementary changes of state

That a change of the state of a body is often connected with a change of the state of another body is an observation of fundamental significance in the study of physical processes. The falling of a clock weight is associated with the concurrent change of state of the mechanism of the clock ; the cooling of a hot block of metal is associated with the heating of a contiguous cold block ; the change of state of exploding gunpowder in a rifle is associated with an ensuing change of state of the bullet and a heating of the rifle barrel.

At the outset of any careful study of such mutually supplementary changes of the states of bodies, it is necessary to establish suitable definitions of the terms to be employed. We require at this stage to make definite what shall be understood by the terms ' body,' ' state,' ' change of state,' and ' supplementary change of state.'

Any material object or assemblage of objects, when no portion of it is removed and no extraneous matter is added to it, shall be termed a **body**. We may say that a body is an object, the masses of whose independently variable component substances remain unvaried. A mass of air, a quantity of brine together with an overlying layer of water vapor, and any closed receptacle together with its contents, are bodies. During the process of heating coexistent brine and vapor contained in a closed receptacle, the layer of brine is not a body ; for a portion of this object is removed in the concurrent evaporation. Unit mass of a mixture of alcohol and water of varying composition is not a body ; for the masses of the independently variable component substances of this object do not remain unvaried.

When a body is participating in no physical process — when its physical character undergoes no alteration — the body shall be said to be in a quiescent **state**. Further, by the ' state ' of a body shall always be understood a quiescent state. This convention will be found to save many words. In the present discussion, the meaning of the term ' state ' shall not be broad-

ened to include either what might be called a ' steady state,' as that of a disc rotating about an axis under the action of constant forces, or what might be called a ' turbulent state,' as that of an exploding mass of gunpowder, or as that of a mass of water in which currents are moving and differences of temperature are being equalized.

When a body passes, in any way, from any given state to any other state, it shall be said to undergo a **change of state.** And this change shall be considered to be the same ' change of state,' whatever the manner in which the process occurs. Thus a quiescent mixture of hydrogen and oxygen gases at a given pressure and temperature may be exploded, and the resulting water be brought to a quiescent state at an assigned pressure and temperature ; or the mixture may first be cooled to the temperature of melting ice, and then exploded and brought to the assigned final state. In both cases the body concerned undergoes the same ' change of state.'

When a body undergoes a change of state in different ways, it shall be said that the **path** of the change of state is different in the different cases. The path of an actual change of state is the actual succession of ' non-quiescent states.' A continuous succession of quiescent states is a mathematical notion, and is termed a **reversible path.**

With reference to a given physical process, the assemblage of all the bodies participating in the process shall be termed the **isolated** body. A change of the state of an isolated body may or may not involve changes of the state of more than one body. If the isolated body is a mass of gas, and its change of state is an abrupt expansion into an exhausted space, only one body is concerned in the process. But suppose the isolated body to be the mass of gas, together with a cylinder and heavy piston confining the gas ; and the change of state to be an expansion of the gas together with a rise of the piston and a cooling of all the three bodies involved — the gas, the cylinder, and the piston. Here the change of state of the isolated body may be considered to consist of changes of the states of these three bodies ; or we may regard it as consisting of the change of state of any one of the three, together with the change of state of the body composed of the assemblage of the other two.

Whenever, as in this illustration, a change of the state of an isolated body can be regarded as consisting of changes of the states of two bodies, each of these two changes of state shall

be said to *supplement* the other.   With reference to any given change of the state of any body, the **supplementary change of state** is the associated change of the state of the body composed of all the other bodies in any way participating in the process.

Nothing that has here been adduced entitles us to assume that a given change of state can always be associated with the same supplementary change of state.   If a change of state A occurring on the path a is supplemented by a change of state B occurring on the path b, we are not at liberty to assume that the change A occurring on another path α can be supplemented by the change B occurring on any path whatsoever.

5. Mechanical aspects of changes of state

Many, possibly all, actually occurring physical processes present a mechanical side.   A rise of temperature, for example, results from friction in a mechanism ; electric effects follow the application of mechanical power to a dynamo ; an excited electromagnet lifts a mass of iron ; expanding steam drives a locomotive ; exploding gunpowder imparts motion to a bullet ; the electrochemical action of a voltaic cell rings a doorbell.   Because the mechanical aspect of a physical process is the aspect that we can most readily formulate in a quantitative way, we are led to seek a quantitative formulation of non-mechanical and of partly-mechanical processes through examination of the relations that these processes bear to mechanical changes of state.

In the development of this idea, a general observation of fundamental importance is that many non-mechanical or partly-mechanical changes of state either are or can be *supplemented* by mechanical operations.   There are two distinguishable ways in which such processes can be thus supplemented :

I. **Directly,** without intervention of any intermediate change of state.   As when the fall or rise of a heavy piston supplements the compression or expansion of a fluid — with a consequent change of the temperature and density of the fluid.

II. **Indirectly,** through shock or through intervention of friction.   As when the temperature of a mass of liquid is raised by stirring it, or when through friction a block of metal is heated or a mass of ice is melted.

Many changes of state can indeed be indirectly supplemented by mechanical operations in other ways, as through interven-

tion of electric or magnetic apparatus, or of radiation phenomena. Such cases, however, shall for the present be omitted from consideration. In the following discussion, by 'indirectly supplemented' shall be invariably meant 'supplemented through intervention of friction,' the friction being understood to occur between solid rubbing surfaces, or between a solid body and a liquid that is stirred by it.

We shall now consider successively some typical cases in which changes of state can be brought into exclusive connection with mechanical operations. Five types of change are to be distinguished. In these, successively, a change of state :

(1) Is *directly* supplemented by a mechanical operation ;
(2) Is or can be *indirectly* supplemented by a mechanical operation ;
(3) Is not and cannot be supplemented, directly or indirectly, by a mechanical operation ; but can be *replaced* by a mechanical operation acting through intervention of friction ;
(4) Is *directly* supplemented in part by a mechanical operation ; and for the rest is or can be *indirectly* supplemented by a mechanical operation ;
(5) Is *directly* supplemented in part by a mechanical operation ; and for the rest is not and cannot be supplemented, directly or indirectly, by a mechanical operation ; but can be *replaced* by a mechanical operation acting through intervention of friction.

We shall now proceed to examine, in order, these five types of changes of state that can be brought into connection with mechanical operations.

Case 1. — A change is directly supplemented by a mechanical operation

Suppose a mass of gas, or coexistent masses of a liquid and its vapor, in a quiescent state in a vertical cylinder under a heavy piston capable of motion without friction. If the pressure exerted by the elastic fluid is not counterbalanced by the weight of the piston, a compression or expansion of the fluid will ensue, and this change of state may be supposed supplemented by the concurrent change of the level of the piston. In this case, the change of the state of the fluid is supplemented by a mechanical operation. The change of state of the fluid

involves an alteration of density and temperature, and possibly a partial evaporation or condensation. In the supplementary change of state, the piston loses or gains a definite quantity of mechanical energy. This state of affairs shall be described by saying that the positive or negative quantity of mechanical energy developed by the piston is added to the fluid. In general :

DEF. *When a change of the state of a body is directly supplemented by a mechanical operation, the positive or negative mechanical energy developed in the mechanical operation is the* **quantity of mechanical energy added** *to the body.*

FIG. 2.

We leave open the question whether the quantity of mechanical energy added depends either on the path of the change of state or on the nature of the supplementary change of state.

If, in the illustration, the mechanical operation is a decrease of the level of the piston, the mechanical energy of the piston at any moment will be the sum of the potential and kinetic energies of this body. If it be supposed that the piston comes to rest after four oscillations (due to the inertia of the mass), the relation between the potential energy, the kinetic energy,

and the total energy of the piston, and the mechanical energy added to the fluid, will be somewhat as represented in Fig. 2. The fall of the piston of weight w from the height $h = 18$ to the height $h = 10$ results in addition of the mechanical energy $w(18 - 10)$ to the fluid.

Case 2. — A change is or can be indirectly supplemented by a mechanical operation

In the absence of a supplementary change, a mass of potassium sulphocyanate dissolving in a mass of water will attain a temperature below the initial temperature of the two-component body.   Suppose occurring at constant volume, or practically so, a rise of the temperature of a block of metal, the fusion of a solid body, the evaporation of a liquid one, or the dissolving of a mass of potassium sulphocyanate in a mass of water under the condition that the initial and final temperatures of the body shall be the same.   Each of these changes of state can be supplemented by an isometric * fall of the temperature of another body, or indeed by any one of a variety of changes of state. Also each of these changes can be supplemented by a mechanical operation acting through intervention of friction, can be 'indirectly supplemented' by a mechanical operation.   The mechanical operation will develop a positive quantity of mechanical energy.   This state of affairs shall be described by saying that the energy developed in the mechanical operation is added to the body undergoing the supplemented change of state.   And the form of description shall be that prescribed by the following definitions.

DEF. *When a change of the state of a body is indirectly supplemented by a mechanical operation, the mechanical energy developed in the mechanical operation is the* **quantity of mechanical energy added** *to the body.*

DEF. *When a change of the state of a body is not, but can be, indirectly supplemented by a mechanical operation, the mechanical energy developed in the mechanical operation is the* **quantity of heat added** *to the body.*

The idea of a 'quantity of heat,' as here introduced, is not to be understood in any sense other than that specified in the definition.   Especially is no hypothetical interpretation to be

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* Occurring at constant volume.

given to it. It is not to be interpreted as a quantity of an imponderable fluid, or as a quantity of kinetic energy of hypothetical particles, or as *any* concept other than that presented by the definition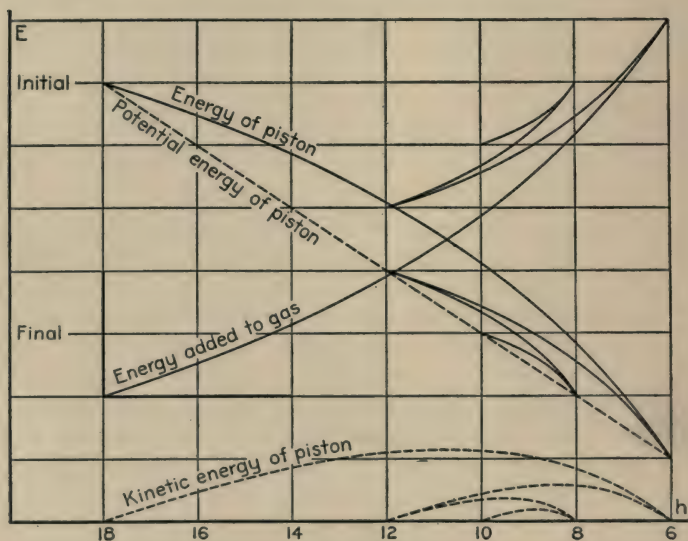. And we leave open the question whether the quantity of heat added depends either on the path of the change of state or on the nature of the supplementary change of state.

Case 3. — *A change is not and cannot be supplemented, directly or indirectly, by a mechanical operation; but it can be* **replaced** *by a mechanical operation acting through intervention of friction*

In the absence of a supplementary change, a mass of sulphuric acid, H_2SO_4, dissolving in a mass of water will attain a temperature above the initial temperature of the two-component body. A chemical reaction in which, in absence of a supplementary change, the changing body attains a temperature above its initial temperature is an 'exothermal' reaction. Suppose occurring at constant volume, or practically so, a fall of the temperature of a block of metal, the solidification of a mass of liquid, the condensation of a mass of vapor, the mixing of a mass of sulphuric acid with a mass of water under the condition that the initial and final temperatures of the body shall be the same, or any exothermal reaction occurring subject to this condition. Each of these changes of state can be supplemented by an isometric rise of the temperature of another body, or indeed by any one of a variety of operations. No one of these changes of state can be supplemented by a mechanical operation, either directly or indirectly; but the actual rise of temperature or other operation that *does* supplement it can in every case be indirectly supplemented by a mechanical operation. In other words, the change itself can be *replaced* by a mechanical operation acting through intervention of friction. This mechanical operation will develop a positive quantity of mechanical energy. This state of affairs shall be described by saying that the energy developed in the mechanical operation is the quantity of energy developed in the change of state that the mechanical operation can replace. And the form of description shall be that prescribed by the following definition:

DEF. *When a change of the state of a body can be replaced by a mechanical operation acting through intervention of friction,*

the mechanical energy developed in the mechanical operation is the **quantity of heat developed** *by the body.   The negative of this quantity is the 'quantity of heat added' to the body.*

We leave open the question whether the quantity of mechanical energy developed in the mechanical operation depends either on the path of the replaced change of state or on the nature of the supplementary change of state.

Cases 4, 5. — A change of state is or can be directly supplemented in part by a mechanical operation; and for the rest can be **indirectly** *supplemented by a mechanical operation, or can be* **replaced** *by a mechanical operation acting through intervention of friction*

Under a heavy piston a mass of gas or a mass of coexistent liquid and vapor is confined in a vertical cylinder standing on a hot block of metal.   The fluid expands, under the constant pressure of the piston.   This change of state is supplemented in part by the mechanical operation of the piston, and for the rest (due to the cooling of the block) it can be indirectly supplemented by a mechanical operation.   Again, a block of ice having the volume V_2 is contained in an open vessel standing on a hot block.   When the ice is melted, its volume is $V_1 < V_2$. The change of state is supplemented in part by the mechanical action of the atmosphere, which adds to the water the mechanical work $p(V_2 - V_1)$, where p is the atmospheric pressure; and for the rest the change can be indirectly supplemented by a mechanical operation.   If in each of these cases the hot block should be replaced by a sufficiently cold one, the change of state would be reversed.   The fluid would contract, under a constant pressure; and the liquid water would solidify, under the pressure of the atmosphere.   In each case, the change of state would be supplemented in part by a mechanical action, and for the rest (in effecting the heating of the block) it could be *replaced* by a mechanical operation acting through intervention of friction.   A similar state of affairs would obtain in the case of an exothermal chemical reaction involving any mechanical effect.

In an attempt to extend to such cases the ideas of additions of quantities of mechanical energy and of heat, we may for the moment confine our attention to a thoroughly typical case.   In a horizontal cylinder, two masses of gas, A and B, are separated

by a light, rigid, thermally conducting piston capable of motion with negligible friction. The two masses have the same initial temperature, but different initial pressures, $p_a > p_b$. The gas A expands and cools; the gas B is compressed and its temperature rises. Spontaneous equalization of these temperatures increases the pressure of A and decreases that of B, thus extending the process.

When the process is completed, A has developed a quantity of mechanical energy M, which may be regarded as having been transferred to B. For the actually occurring change of volume of A can be supposed replaced, in so far as the influence of this change of volume upon B is concerned, by the change of state of a mechanism acting upon the piston. The change of state of the gas A is supplemented by a change of state (that of the gas B), whose action is in part that of a mechanical operation absorbing the mechanical energy M, and whose action for the rest is that of a mechanical operation acting through intervention of friction. The (negative) quantity of mechanical energy developed by B shall be termed the *quantity of mechanical energy* developed by B and added to A; and the mechanical energy developed by the mechanical operation acting through intervention of friction shall be termed the *quantity of heat* developed by B and added to A.

The general case

The statements and definitions of this detailed examination of the mechanical aspects of changes of the physical states of bodies may now be summarized, as follows:

STMT. *Many supplemented changes of the physical states of bodies can be brought directly or indirectly, or both directly and indirectly, into exclusive connection with mechanical operations. Every such change of state is directly supplemented, wholly or in part or not at all, by a mechanical operation; and, in so far as it is not so supplemented, it either is or can be supplemented by a mechanical operation acting through intervention of friction, or it can be replaced by a mechanical operation acting through intervention of friction.*

DEF. *When two bodies undergo mutually supplementary changes of state of the class described, the quantity of mechanical energy developed by either one of the bodies is the* **quantity of mechanical energy added** *to the other.*

And the mechanical energy developed in the mechanical opera-tion that can for the rest supplement one of the changes of state and replace the other, on the actual paths of these changes of state, is the **quantity of heat added** *to the body undergoing the sup-plemented change of state, and is the negative of the quantity of heat added to the body undergoing the replaced change of state.*

In the establishment of these definitions we leave open the question whether the quantities of mechanical energy and of heat added to a body in a change of its state depend either on the path of the change of state or on the nature of the supple-mentary change of state. It is readily seen, however, that *in general* these quantities are certainly not independent of the *path* of the change of state. This may be shown by an example. The state of a given mass of coexistent liquid and vapor is de-termined by the volume V and the temperature τ of the mass. Under the constant pressure determined by the initial state, let the state change from V_a, τ to V_b, τ where $V_b > V_a$. The body develops a quantity of mechanical energy M_1, and absorbs a quantity of heat Q_1. Again, let the body pass from its initial state to a state in which its volume is V_b, by abrupt expan-sion into an adjoining vacuum $V_b - V_a$. The temperature will fall thereby, whereupon the state V_b, τ can be reached on addition of a quantity of heat Q_2. On the first of these two paths the quantity of mechanical energy M_1 is added to the body ; on the second path the mechanical energy added is zero. And it can be experimentally shown that the quantities of heat Q_1, Q_2 are not equal.

6. Thermodynamic changes of state

The present discussion is concerned with supplemented changes of state, not purely mechanical, that can be brought directly or indirectly or both directly and indirectly into con-nection with mechanical operations. The states of any given body, attainable through changes of state of this class, consti-tute the continuous assemblage of the **thermodynamic states** of the body. All such changes of state, and also all possible changes of the state of any *isolated* body from one thermody-namic state to another, are termed **thermodynamic changes of state.** The study of thermodynamic changes of state is **ther-modynamics.**

Many changes of the physical states of bodies can be sup-

plemented or replaced in part by mechanical operations acting
through intervention of friction, and in part by mechanical
operations acting indirectly in other ways, as through interven-
tion of the action of electric or magnetic apparatus or of radia-
tion.   Such changes of state must indeed be regarded as in-
cluded in the province of thermodynamics understood in a
broad sense.   But their study is an *extension* of the principles
of thermodynamics to a domain lying beyond the immediate
province of the subject, and it cannot conveniently be entered
upon until after this immediate province has been surveyed.

Thermodynamic processes, like mechanical processes, are ab-
stractions.   In either case certain features of a process, ab-
stracted from the actual phenomena, constitute the subject of
study.   Purely thermodynamic operations, like purely mechan-
ical operations, do not exist.   A mechanical operation is com-
plicated by unavoidable friction, or electrostatic attractions,
and the like ; and a thermodynamic operation involves features
of radiation and what not.   In any case it is an ideal, abstract
process that is the subject of study ; but the disparity between
it and the corresponding actual physical operation is kept as
small as possible.

7. Summary of Chapter I.

Thermometry

We distinguish different degrees of hotness.   Any measurable
physical property of a body, that is a continuous, uniform, and
increasing (or decreasing) function of the degree of hotness of
the body, is a *thermometric property* of the body.   Successive
values of a thermometric property of a given body afford an
arbitrary scale of the 'temperatures of a thermometer.'   With
reference to this scale, the *temperature* of another body can be
determined by establishing temperature equilibrium between the
body and a thermometer.   A *reproducible* scale of temperatures
is established if the temperature is defined by any uniform,
analytic, and increasing (or decreasing) function of a chosen
thermometric property of a chosen *substance*.   Such a scale is
that of the temperatures

$$\tau = \frac{273}{v_0}\, v$$

of a constant pressure gas-thermometer, the definition of which

is suggested by the 'law of Gay-Lussac.' A body permitting rapid equalization of the temperatures of bodies contiguous with it is a 'thermally conducting' body ; one permitting only a very slow equalization of these temperatures is a 'thermally non-conducting' body.

Physical Processes

An ensemble of changes of the physical properties of an assemblage of bodies is a 'physical process.' Physical processes may be classified in accordance with the degree in which the physical character of the participating bodies is modified. Of all physical happenings, the mechanical processes are the *least* deep-seated. The way in which they occur is better understood than is the way in which any other physical processes occur. In any purely mechanical process the sum of the potential and kinetic energies of the participating bodies remains constant.

Supplementary Changes of State

A *body* is an object, the masses of whose independently variable component substances remain unvaried. When the physical character of a body undergoes no alteration, the body is said to be in a (quiescent) physical *state*. When the body passes from one state to another it undergoes a definite *change of state*. The *path* of an actual change of state is the actual succession of 'non-quiescent states.' A continuous succession of quiescent states is a mathematical notion, and is termed a *reversible path*. With reference to any given change of the physical state of any body, the *supplementary change of state* is the associated change of state of the body composed of all the other bodies in any way participating in the process. It may not be assumed that a given change of state can always be associated with the same supplementary change of state.

Mechanical Aspects of Changes of State

Many supplemented changes of the physical states of bodies can be brought 'directly' (without intervention of an intermediate change of state), or 'indirectly' (through intervention of friction), or both directly and indirectly, into exclusive connection with mechanical operations. Every such change of state is directly supplemented, wholly or in part or not at all, by a

mechanical operation ; and, in so far as it is not so supplemented, it either is or can be supplemented by a mechanical operation acting through intervention of friction, or it can be replaced by a mechanical operation acting through intervention of friction.

DEF. When two bodies undergo mutually supplementary changes of state of the class described, the quantity of mechanical energy developed by either one of the bodies is the *quantity of mechanical energy added* to the other. And the mechanical energy developed in the mechanical operation that can for the rest supplement one of the changes of state and replace the other, on the actual paths of these changes of state, is the *quantity of heat added* to the body undergoing the supplemented change of state, and is the negative of the quantity of heat added to the body undergoing the replaced change of state.

In general, the quantities of mechanical energy and of heat added to a body in a change of its state are not independent of the path of the change of state.

Thermodynamic Changes of State

The present study is concerned with supplemented changes of state, not purely mechanical, that can be brought directly or indirectly or both directly and indirectly into exclusive connection with mechanical operations. The states of any given body, attainable through such changes of state, constitute the continuous assemblage of the *thermodynamic states* of the body. All such changes of state, and also all possible changes of the state of any *isolated* body from one thermodynamic state to another, are termed *thermodynamic changes of state*. The study of thermodynamic changes of state is *thermodynamics*.

CHAPTER II. The First Law of Thermodynamics

1. The problem

The conclusion of the foregoing discussion may be stated to be that all thermodynamic changes of state can be brought into exclusive connection with operations of a wholly mechanical character, that all such changes can be supplemented or replaced — or both supplemented and replaced — by mechanical operations.

As has been stated, we seek to attain a quantitative formulation of thermodynamic changes of state through examination of the relations that these operations bear to mechanical changes of state.

In purely mechanical processes, the total mechanical energy of the participating bodies remains constant. This fact offers a promising suggestion. It leads us to enquire whether a physical quantity, the 'energy of a body,' can be defined in such a way that the total energy of the bodies participating in any thermodynamic process will remain constant. The present chapter is a consideration of this question.

If it can be shown that the 'energy of a body,' thus established by definition, is uniquely determined by the state of the body ; and if then the energies of the bodies participating in a thermodynamic process can be analytically expressed by means of independent measurable physical quantities determined by the thermodynamic states of the bodies ; we shall thereby obtain analytical *relations* between such physical variables. These relations will quantitatively describe the thermodynamic changes of state of the bodies. They will thus constitute, at least in some measure, a *rational theory* of thermodynamics.

2. A definition

If it is possible to define the 'energy of a body' in such a way that the sum of the energies of the bodies participating in any thermodynamic process remains constant, the 'change of the energy' of a body undergoing a change of thermodynamic state must be defined in such a way that :

a) If the change of state is or can be supplemented, directly or indirectly or both directly and indirectly, by mechanical

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operations, the change of the energy of the body and the total change of the mechanical energies of the bodies executing the mechanical operations must be equal and have opposite signs. *I. e.*, the change of the energy of the body must be equal to the algebraic sum of the quantities of mechanical energy and of heat added to the body.

b) The changes of the energies of two bodies undergoing mutually supplementary changes of thermodynamic state must be equal and have opposite signs. *I. e.*, the change of the energy of a body undergoing *any* supplemented change of thermodynamic state must be equal to the algebraic sum of the quantities of mechanical energy and of heat added to the body.

c) The change of the energy of any isolated body undergoing a change of thermodynamic state must be zero, — whether the change of state does or does not consist of mutually supplementary changes of state.

In short, if the 'energy of a body' *can be* defined in such a way that the sum of the energies of the bodies participating in any thermodynamic process will remain constant, it must be defined by means of its *changes*, and in the following fashion :

DEF. The **change of the energy**, U_{ab}, of a body undergoing a change of thermodynamic state from the state *a* to the state *b* is equal to the algebraic sum of the quantities of mechanical energy M_{ab} and heat Q_{ab} added to the body in the course of its change of state,

$$U_{ab} = M_{ab} + Q_{ab}.$$

3. Necessary conditions

It is now to be enquired whether any 'change of the energy' of a body is the change of a quantity $E_x + E_o$ whose value, save for an additive constant E_o, is uniquely determined by the thermodynamic state *x* of the body ; whether

$$(1) \qquad U_{ab} = (E_x + E_o)\Big|_a^b$$
$$= E_b - E_a.$$

We proceed to examine the conditions that must be fulfilled in order that the relation (1) shall be satisfied.

It must first be shown that given transfers of mechanical energy and of heat are definite quantities. It must be shown that in any recurrence, on a given path, of a thermodynamic

process consisting of given mutually supplementary changes of
the states of bodies, the quantity of mechanical energy trans-
ferred from one body to the other is always the same, and the
quantity of heat transferred from one body to the other is always
the same.   If it should be shown that these conditions are ful-
filled, it would be shown that the change of the energy, U_{ab}, of
a body has always the same value when the change of thermo-
dynamic state ab occurs on a given path with a given supple-
mentary change of state.

Yet the change of energy U_{ab} might vary with the *path* of
the change of state.   Suppose a mass of gas, whose thermo-
dynamic state is determined by its pressure p and volume V,
confined under a piston in a vertical cylinder resting on a metal
block.   Let the mass change from the state $a = p_1,\ V_1$ to the
state $b = p_1,\ V_2$; this change of state being supplemented by a
cooling of the block through the temperature interval $\tau_2 - \tau_1$,
together with a rise of the piston through the increment of
height $h_2 - h_1$.   On this ' path I,' the change of energy U_{ab} of
the gas is the algebraic sum of the
negative mechanical energy devel-
oped by the piston and the positive
heat developed by the block.   On
a ' path II,' let the gas change from
its initial state to the state $p_2,\ V_1$;
the change being supplemented by
a cooling of the block of metal
through the temperature interval
$\tau_2 - \tau_1'$; whereupon ensues a con-

cluding change (adiabatic expansion) to the state $p_1,\ V_2$, sup-
plemented by a rise of the piston through the increment of
height $h_2 - h_1$.   Will it be observed that $\tau_1 = \tau_1'$?   For these
temperatures must be the same if the quantity U_{ab} have the
same value with reference to both paths.
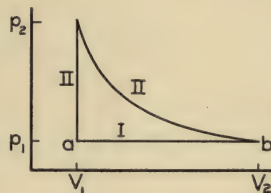
If it should be shown that U_{ab} *is*, in general, independent of
the path of the change of state, this quantity might yet vary
with the *supplementary change* of state.   For example, in the
above illustration, let the change of state of the gas, occurring
on the path I, be supplemented by a rise of the piston from h_1
to h_2, together with a mixing of certain quantities of sulphuric
acid and water, the initial and final temperatures of this body
being the final temperature of the gas.   Will it be observed
that the quantity of mechanical energy expended, through inter-

vention of friction, to replace the mixing, is equal to that requisite to replace the cooling of the block from τ_2 to τ_1? For these quantities of mechanical energy must be equal, if the quantity U_{ab} is to have the same value in both cases.

4. Sufficiency of the conditions

If it should be shown to be true that the change of energy U_{ab} of a body undergoing any change of thermodynamic state ab is independent of the path of the change of state, and is independent of the supplementary change of state, it would thereby be shown that the quantity U_{ab} is uniquely determined by the end states of the body. And it would follow that the change of energy U_{ab} is equal to the concurrent change of a quantity $E_x + E_o$ whose value, save for an arbitrary additive constant E_o, is uniquely determined by the thermodynamic state x of the body.

For, if o, a, b be any three states of any given body, we should have

$$U_{oa} = M_{oa} + Q_{oa}$$

$$U_{ab} = M_{ab} + Q_{ab};$$

whence

$$U_{oa} + U_{ab} = (M_{oa} + M_{ab}) + (Q_{oa} + Q_{ab}).$$

The second member of this equation, being the total mechanical energy and the total heat absorbed in any two consecutive paths oa, ab, would be the change of energy U_{ob} of the body undergoing the change of state from o to b. Therefore,

$$U_{oa} + U_{ab} = U_{ob};$$

and, hence,

$$U_{ab} = U_{ob} - U_{oa}.$$

Taking the state o as a fixed state of reference, U_{ob} would be determined by the state b, and U_{oa} by the state a. So U_{ab} would be equal to a quantity determined by b, less a quantity determined by a. It follows that U_{ab} would be equal to the concurrent change of the value of a quantity $E_x + E_o$ uniquely determined by the thermodynamic state of the body; though E_x might be determined in different ways in different contiguous regions of state.

5. The first law of thermodynamics

In the experimental study of thermodynamic processes, there have been made very extended and careful measurements of the quantities of mechanical energy and of heat transferred between bodies undergoing mutually supplementary changes of state. In some experiments, mechanical operations have supplemented changes of the temperatures of bodies, and changes of their states of aggregation. In other experiments, conducted in 'calorimeters,' changes of temperature, changes of states of aggregation, the formation of homogeneous liquid mixtures from separate liquids or from liquids and solids, chemical changes of state, and combinations of these, have supplemented changes of the temperatures of other bodies, and sometimes mechanical actions as well. The results obtained in an immense number of such experiments give extensive support to the hypothesis that the algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is independent of the supplementary change of state and of the path of the change of state.

These results therefore lead to the conclusion that :

The algebraic sum of the mechanical energy and heat added to a body undergoing a change of thermodynamic state is equal to the concurrent change of a quantity whose value, save for an arbitrary additive constant, is uniquely determined by the thermodynamic state of the body,

$$M_{ab} + Q_{ab} = (E_x + E_o)\Big|_a^b$$

$$= E_b - E_a.$$

This hypothesis is the **first law of thermodynamics.** The quantity $E_x + E_o$ is the **energy** of the body. Unless otherwise stated, the 'energy' of a body shall hereafter be understood in this sense. The quantity $E_x + E_o$ is sometimes termed the 'inner energy' of the body, to distinguish it from the kinetic and potential energies, whose sum is the mechanical energy of the body, or from the energy due to an electrostatic charge or to other actions. The justification of the first law of thermodynamics lies largely in the agreement of its consequences with experience. This agreement is very extended and exact.

The law involves the statement that the algebraic sum of the

changes of the energies of bodies undergoing mutually supplementary thermodynamic changes of state is zero; or, more generally, that the energy of an isolated body undergoing any change of thermodynamic state is constant. This form of statement is the **law of the conservation of energy,** as applied to thermodynamic processes.

6. The calory

The numerical value of a quantity of heat transferred from one body to another is determined by the quantity of mechanical energy developed in a mechanical operation. This mechanical operation can supplement a rise of the temperature of a body of water. The mass of the body of water whose temperature is thus raised through a fixed interval $\tau - \tau_r$ is proportional to the quantity of mechanical energy developed in the mechanical operation. So this mass is an expression of the quantity of heat transferred from the one body to the other. The heat-unit determined by the quantity of mechanical energy requisite to raise unit mass of water through the interval $\tau - \tau_r = 1$, from an assigned temperature τ_r (usually 15° C.) on a given scale of temperatures, is termed the **calory**. The calory is practically identical with the 'specific heat' of water at the assigned temperature; though, strictly, the specific heat of a substance is the quantity of heat absorbed, by unit mass of the substance, *per* unit increase of the temperature of the mass. Strictly, the specific heat of a substance is defined with reference to a given path, and is a *rate*. When expressed in mechanical units, the calory is often termed the **mechanical equivalent of heat**.

7. Scholium

In considering transfers of heat, it is well to bear in mind that positively "adding heat" to a body — "heating the body" — is not in general associated with a rise of the temperature of the body. When heat is added to a block of metal, the temperature of the block rises. When heat is added to a mass of liquid water and overlying water vapor supporting a constant pressure, the temperature of the mass is not altered. Heat may be added to a mass of potassium sulphocyanate and water, in the process of forming a mixture, and the temperature fall. An addition of heat to a body involves a change of the state of the body; but it may not involve a change of the temperature

alone, and it may not involve a change of the temperature at all. Contrariwise, a change of the temperature of a body does not necessarily involve absorption or development of heat. When a mass of air is adiabatically * compressed, or when it expands into a vacuum, the temperature of the mass changes, but no heat is added to it.

8. Summary of Chapter II.

The Fundamental Problem

The thesis of Chapter I. is that all thermodynamic changes of state can be supplemented or replaced — or both supplemented and replaced — by mechanical operations. We seek to establish a quantitative formulation of thermodynamic changes of state, through examination of the relations that these operations bear to mechanical changes of state. Can this end be attained through defining the 'energy of a body' in such a way that the total energy of the bodies participating in any thermodynamic process will remain constant? So defined :

DEF. The energy of a body in any thermodynamic state x is a quantity $E_x + E_o$, whose change U_{ab} when the body undergoes a change of thermodynamic state from the state a to the state b is equal to the algebraic sum of the quantities of mechanical energy M_{ab} and heat Q_{ab} added to the body in the course of its change of state,

$$U_{ab} = M_{ab} + Q_{ab}.$$

It remains to be determined whether the quantity U_{ab} is really equal to the change of a quantity $E_x + E_o$ whose value, save for an arbitrary additive constant E_o, is uniquely determined by the thermodynamic state x of the body ; whether

$$U_{ab} = (E_x + E_o) \Big|_a^b.$$

To establish that U_{ab} is equal to the change of such a quantity, it is necessary to establish that U_{ab} is determined by the states a,b ; it is necessary to establish that U_{ab} is independent of the path of the change of state ab, and of the supplementary change of state.

The necessary condition, that U_{ab} is determined by the states

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* Without transfer of heat to or from the mass.

a,b is also the sufficient condition.   For, if this condition is fulfilled, with regard to any paths oa, ab we shall have

$$U_{oa} = M_{oa} + Q_{oa}$$

$$U_{ab} = M_{ab} + Q_{ab};$$

whence,

$$U_{oa} + U_{ab} = (M_{oa} + M_{ab}) + (Q_{oa} + Q_{ab})$$

$$= U_{ob}.$$

Hence,

$$U_{ab} = U_{ob} - U_{oa}.$$

Taking the state o as a fixed state of reference, U_{ob} is determined by the state b, and U_{oa} by the state a.   So U_{ab} is equal to a quantity determined by b, less a quantity determined by a. It follows that U_{ab} is equal to the concurrent change of the value of a quantity $E_x + E_o$ uniquely determined by the thermodynamic state of the body; though E_x may be determined in different ways in different contiguous regions of state.

The First Law

Extended and careful experimental study has been made of thermodynamic processes in which mechanical operations supplement changes of the temperatures and changes of the states of aggregation of bodies, and of processes in which various changes of thermodynamic state supplement changes of the temperatures of other bodies and often mechanical actions as well.   The results obtained in an immense number of such experiments give extensive support to the hypothesis that the algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is independent of the supplementary change of state, and of the path of the change of state.

These results therefore lead to the conclusion that: The algebraic sum of the mechanical energy and heat added to a body undergoing a change of thermodynamic state is equal to the concurrent change of a quantity whose value, save for an arbitrary additive constant, is uniquely determined by the thermodynamic state of the body,

$$M_{ab} + Q_{ab} = (E_x + E_o)\Big|_a^b$$

$$= E_b - E_a.$$

This conclusion is the *first law of thermodynamics*. The quantity $E_x + E_o$ is the *energy* of the body. The *justification* of the first law of thermodynamics lies largely in the extended and exact agreement of its consequences with experience.

The Calory

The heat unit determined by the quantity of mechanical energy requisite to raise unit mass of water through the interval $\tau - \tau_r = 1$ is termed the *calory*. The calory is practically identical with the specific heat of water at τ_r (usually 15° C.). When expressed in mechanical units it is known as the *mechanical equivalent of heat*.

CHAPTER III. The Second Law of Thermodynamics

1. The problem

In order to express the first law of thermodynamics,

$$E_b - E_a = M_{ab} + Q_{ab},$$

by means of quantities determined by the thermodynamic state of the body undergoing the change of state ab, it is necessary to express each of the terms M_{ab} and Q_{ab} by means of such quantities.

The first of these terms, the quantity of mechanical energy M_{ab} added to the body, can readily be expressed in this way when the path of the change of state ab is a *reversible* path,— when it is a continuous succession of thermodynamic 'states.' For, in this case, the positive or negative quantity of mechanical energy added is the *work* W_{ab} of the forces supported by the body. The work of such a force is the product of the force into the effected displacement; and, at every point of the path, the force is counterbalanced by a force exerted by the body. The force and the displacement are quantities that are determined by the thermodynamic states of the body.

A reversible change of state, to be sure, is a mathematical process and not a physical one. Yet a reversible path can in general be closely approximated by an actual path conducted with great slowness; and the study of reversible processes leads to a very interesting theory of the equilibrium and stability of thermodynamic states.

The formulation of reversible additions of work to a body may be illustrated as follows. In a reversible compression, let the force acting on unit area of the compressed body be a uniform and normally directed pressure. The pressure supported by the body is the pressure p 'of the body'; and the work

$$W_{ab} = - \int_a^b p \delta V$$

added to the body on an assigned reversible path is the limit, with regard to this path, of the sum of successive small additions of work $- p \delta V$, when the successive volume decrements

— δV are made to vanish. This limit may be represented by an area in a diagram whose rectangular coördinates are p, V. If, now, within the region of states traversed by the path of compression, the physical quantities p, V are expressed as functions of independent measurable physical quantities whose values determine the thermodynamic states of the body ; and if the reversible path is determined by a known relation

$$p = p(V);$$

the work added to the body in the process of compression receives the analytical expression

$$W_{ab} = - \int_{V_a}^{V_b} p(V)dV.$$

Obviously, the quantity of work W_{ab} depends on the form of the function $p(V)$. Depending thus on the path of integration, it is the integral of the *inexact* differential expression
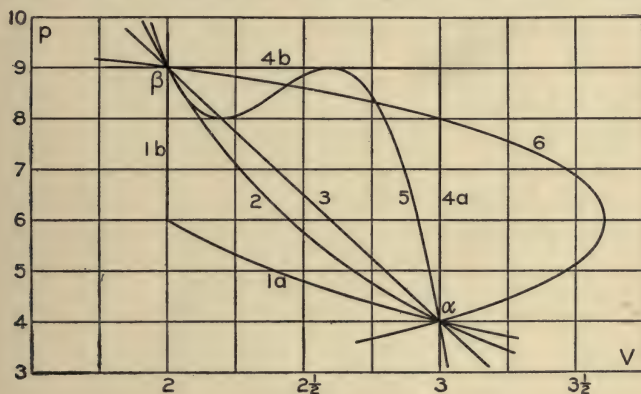
FIG. 4.

— pdV. Suppose, for example, that a given mass of air is brought by reversible compression from the state $p = 4$, $V = 3$, to the state $p = 9$, $V = 2$, i. e., from the state a to the state b in Fig. 4.* And suppose the change of state ab to be effected on six successive paths, determined respectively by the relations

Path 1. $pV = 12$, to $V = 2$; then $V = 2$.

" 2. $pV^2 = 36$.

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* Through an oversight these states are indicated by α and β in the figure.

Path 3. $p = 19 - 5V$.

" 4. $V = 3$, to $p = 9$; then $p = 9$.

" 5. $p = 431.5 - 563.25V + 225V^2 - 31.25V^3$.

" 6. $p = 6 \pm \sqrt{13 - V^2}$.

Indicating the volume limits V_a, V_b by a,b, the quantities of work added to the mass of air on these successive paths are:

$$W_{ab} = -12 \int_a^b \frac{dV}{V} + 0 \qquad = 12 \log \frac{V_a}{V_b} \qquad = 4.87$$

$$= -36 \int_a^b \frac{dV}{V^2} \qquad = 36\left(\frac{1}{V_b} - \frac{1}{V_a}\right) \qquad = 6.0$$

$$= -\int_a^b (19 - 5V)dV = 19(V_a - V_b)$$
$$+ \tfrac{5}{2}(V_b^2 - V_a^2) = 6.5$$

$$= 0 - 9 \int_a^b dV \qquad = 9(V_a - V_b) \qquad = 9.0$$

$$= -\int_a^b p(V)dV \qquad = \left[\frac{31.25}{4}V^4 - \frac{225}{3}V^3 \right.$$
$$\left. + \frac{536.25}{2}V^2 - 431.5V\right]_{V=3}^{V=2} = 8.0$$

$$= -\int_a^b p(V)dV \qquad = \int_2^{\sqrt{13}}(6 + \sqrt{13 - V^2})dV$$
$$+ \int_{\sqrt{13}}^3 (6 - \sqrt{13 - V^2})dV = 10.2$$

Whatever be the forces acting upon a body undergoing a reversible change of thermodynamic state, the work W_{ab} of these forces, as in the above illustrative case, will depend in general on the path of the change of state. Now, we have

$$E_b - E_a = W_{ab} + Q_{ab},$$

where the change of the energy of the body is independent of the path of the change of state. It follows that the positive or negative quantity of heat Q_{ab} added to a body undergoing a reversible change of thermodynamic state depends in general on the path of the change of state. The question arises

whether this transfer of heat can be expressed by means of quantities determined by the state of the body. This is the problem with which the present chapter is concerned.

2. A mechanical analogy

A transfer of heat may be regarded as being a transfer of a quantity of stored work. If an expenditure of work has raised the temperature of a block of metal, and a subsequent cooling of the block transfers a quantity of heat to a contiguous body, the work expended was 'stored' in effecting a change of state of the block, and this stored work is transferred to the contiguous body. A quantity of heat is a quantity of stored work.

When a barrel of flour has been raised from the basement to the n-th floor of a warehouse, the work absorbed by the barrel has been 'stored' as the potential energy of the barrel. When the barrel is transferred from the n-th floor to an elevator, the stored work is transferred to the elevator. And the stored work so transferred is the product of the level of the elevator into the change of its load. In this way, the quantity of potential energy transferred is expressed by means of quantities determined by the state of the elevator.

If, now, a transferred quantity of heat can be regarded as having been produced in some similar way by an expenditure of work, it may prove possible to express the transfer by means of quantities analogous to the level and change of load of the elevator, and so by means of quantities determined by the thermodynamic state of the body to which the heat is added. Let us proceed to examine the possibilities of this idea.

3. Heat transfers and temperature equalization

On transferring a barrel of flour to a freight elevator at the basement floor, transporting the barrel to the n-th floor, and returning the elevator to the basement, a net expenditure of work is converted into a transfer of potential energy at the n-th floor: through a cyclical change of the state of the elevator, an expenditure of work is converted into a transfer of *potential energy* at a given *height*. Through the agency of a cyclical operation, can an expenditure of work be converted into a transfer of *heat* at a given *temperature?*

A transfer of heat to or from a body occurs through the tendency of bodies having different temperatures to attain a com-

mon temperature when they are brought into contact with each other. Thus two contiguous metal blocks at different temperatures will attain thermal equilibrium at an intermediate temperature. When the cooling of a metal block supplements an isothermal evaporation, or when a warming of the block supplements an isothermal condensation of vapor, the block attains the temperature of the evaporating or condensing fluid. When the freezing of a mass of wax at its melting temperature τ_2 supplements the fusion of ice at its melting temperature $\tau_1 < \tau_2$, the two bodies maintain their temperatures until the freezing or the fusion is complete ; whereupon the resulting solid wax or liquid water attains the temperature of the other body.

The operation wherein two contiguous bodies attain a common temperature is a spontaneously occurring process. Now, every actual thermodynamic process is a spontaneously occurring change of the state of a body composed of all the bodies participating in the operation : it is a spontaneous change of the state of an isolated body. And it is an important principle, that every spontaneously occurring thermodynamic process can be utilized for the production of work. Consider a block of metal falling freely from one level to another * ; or a mass of gas expanding freely into a vacuum. By means of a cord running over a pulley, the falling block can be made to raise another block ; by means of a piston in a cylinder, the expanding gas can be made to do work against an opposing pressure. In these cases, as in all others, the maximum work obtainable is obtained when the process is conducted reversibly : the falling block yields the maximum work when it and the lifted block have the same weight ; the expanding gas yields the maximum work when the opposing pressure is equal at each moment to the pressure of the gas. In like wise, when two blocks of metal attain a common temperature, the process is a spontaneous one and can be utilized for the development of work. And the maximum work will be developed when the operation is conducted in a perfectly controlled, or reversible, manner.

Reversible equalization of the initially different temperatures of two blocks of metal can be conducted in the following way. Let a mass of some gas, having the temperature τ_2 of the hot block, and being confined in a cylinder under a piston moving without friction, be brought into contact with the hot block.

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* This is a thermodynamic process ; for at the lower level the potential energy lost by the body is converted into heat.

On reversible expansion, the gas will develop work, and will absorb heat from the hot block, the common temperature of the two bodies falling thereby to $\tau_2 - \delta_1\tau$. Let the cylinder now
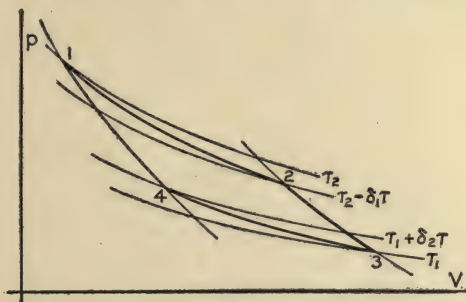
FIG. 5.

be removed from contact with the block, and the gas be adiabatically * expanded until its temperature has fallen to the temperature τ_1 of the cold block. Next, after establishing contact with the cold block, let the gas be reversibly compressed until the path of its change of state, as represented for example in the p, V-diagram, Fig. 5, meets the adiabatic path passing through the point representing the initial state. In this compression the gas absorbs work, and the common temperature of the two bodies rises to $\tau_1 + \delta_2\tau$. Removing the cylinder from contact with the block, adiabatic compression restores the gas to its initial state. In this cycle of operations the gas has reversibly developed the quantity of work represented by the area of the closed figure in the diagram. And the temperature difference of the two blocks is now less than it initially was, by the amount $\delta_1\tau + \delta_2\tau$. On a sufficient number of repetitions of this cyclical operation, the blocks will have been brought to a common temperature; and the maximum work obtainable from the temperature equalization will have been developed. The net result is that the change of state of the metal blocks has been supplemented by a change of state consisting of an absorption of work.

It is easily seen that the heat developed by the hot block is equal to the sum of the heat absorbed by the cold block and the work developed. For, in the succession of cyclical opera-

* 'Adiabatic' changes of the thermodynamic state of a body are changes in which no heat is transferred to or from the body.

tions, the working gas has absorbed the heat Q_2 from the hot block, has developed the heat Q_1 transferred to the cold block, and has developed the work W. Each operation being cyclical, the outstanding change of the energy E of the gas is zero ; so, by the first law of thermodynamics,

$$\Delta E = W + Q$$

$$o = Q_2 - Q_1 - W.$$

It will be remarked that the final temperature of the blocks is not the temperature that would have been attained had the process occurred in a wholly spontaneous way — without development of work. The bearing of this important observation will be made the subject of Chapter V.

It will not be out of place, at this point, to examine in detail the reversible equalization of the temperatures of our blocks by the agency of a succession of cyclical operations. Let the two blocks have the temperatures τ_7 and $\tau_1 < \tau_7$. Let the state of the mass of gas in the cylinder be represented by the point a_1 in Fig. 6. Beginning with expansion in contact
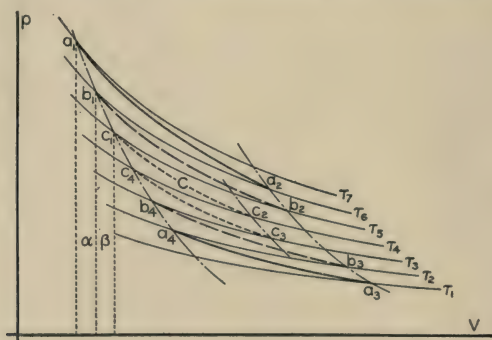
FIG. 6.

with the hot block until the common temperature of the block and the gas has fallen to, say, τ_6, the cycle $a_1 a_2 a_3 a_4$ will bring the cold block to the temperature τ_2. Before repeating the operation, the gas must be brought from its end temperature τ_7 to τ_6. Suppose this done adiabatically, so that only a transfer of *work* will be involved. The work represented by the area α is developed. The cycle $b_1 b_2 b_3 b_4$ will now bring the blocks to the respective temperatures τ_5 and τ_3 ; and in bringing the gas

from τ_6 to τ_5, in preparation for the concluding cycle, the work represented by the area β is developed.

The concluding cycle, which begins with the gas at c_1, must be so conducted as exactly to equalize the temperatures of the two blocks, which now are τ_5 and τ_3. Let C in Fig. 7, in which the concluding cycle is represented alone, be the path of
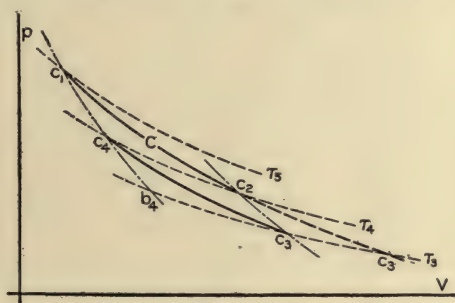
FIG. 7.

expansion of the gas in contact with the hot block. As the representative point moves along C, the adiabatic passing through this point moves with it, as does the intersection of this adiabatic with the isotherm τ_3, as does the line passing through this intersection and representing the path of compression, from the intersection, if the gas were in contact with the cold block. As the representative point moves along C, the intersection of this path of compression with the adiabatic passing through c_1 rises continuously from the point b_4; and the isotherm passing through the representative point falls continuously from τ_5. At some intermediate temperature τ_4, the isotherm of the intersection and the isotherm of the representative point will coincide. The representative point will then be c_2, and the path of compression will be $c_3 c_4$. The cycle $c_1 c_2 c_3 c_4$ will leave the two blocks at exactly the same temperature τ_4.

At the close of this concluding cycle, the state of the auxiliary working body, the gas, is represented by the point c_1 in Fig. 6. Adiabatic compression to the point a_1 will restore the gas to the state it was in at the outset of the series of operations. This absorbs the work represented by the areas a, β, which previously was developed. The net result, now, is that in three cyclical operations the gas has absorbed three quanti-

ties of heat ΣQ_2 at temperatures above τ_4, has developed three quantities of heat ΣQ_1 at temperatures below τ_4, and has developed the work ΣW represented by the areas of the three cyclical figures in the p, V-diagram. Equalization of the temperatures of two metal blocks has been supplemented by a change of state consisting of an absorption of work; and, by the first law of thermodynamics, the energy changes associated with these supplementary changes of state are connected by the relation

$$o = (\Sigma Q_2 - \Sigma Q_1) - \Sigma W.$$

In the form

$$\Sigma Q_2 = \Sigma Q_1 + \Sigma W,$$

this relation may, more figuratively, be considered to assert that the quantity of heat ΣQ_2 absorbed at temperatures above τ_4 has been converted in part into the quantity of heat ΣQ_1 developed at temperatures below τ_4, and in part into the developed work ΣW.

An important question remains. By varying the cycles, can the blocks be reversibly brought to a common temperature different from τ_4? Suppose one succession of cycles to bring them to τ_5. Then less heat than before will be absorbed by the gas, more heat will be developed, and in consequence less work will be developed. We shall have two total processes, one bringing the blocks to τ_4 and developing the work W, the other bringing the blocks to τ_5 and developing the work $w < W$.

Beginning with the blocks at their respective temperatures τ_7, τ_1, let the first process bring them to τ_4 and develop the work W. Then, through contact with some sufficient source of heat, let them be brought to the temperature τ_5. Now, through reversal of the second process, the blocks may be returned to their initial state. There remains a change consisting of an absorbtion of the work W — w, supplemented by a fall of the temperature of a body of uniform temperature. But this is inadmissible. If a fall of the temperature of a body of uniform temperature could supplement an absorption of work, it would be possible to construct a motor that should function at the expense of a cooling of the atmosphere or of the sea. This possibility cannot be admitted. It must therefore be concluded that reversible equalization of the temperatures of the blocks, whatever the paths of the auxiliary cyclical operations, will always bring the blocks to the same common final temper-

ature, and will always develop the same amount of work — the maximum that the spontaneous process of temperature equalization can supply.

A reversal of this operation would result in causing an expenditure of work to effect a *separation* of the temperatures of the two metal blocks. In each of the reversed cyclical operations, the temperature of one of the blocks would fall, that of the other would rise, and a positive quantity of work would be absorbed. A change of state consisting of a development of work would supplement the change of state of the two blocks. Here again the equation formulating the change of the energy of the working gas shows that the sum of the supplied work and the heat developed by the cooling block is equal to the heat absorbed by the block whose temperature is raised,

$$o = W + Q_1 - Q_2.$$

It may be considered that the work supplied is converted into a portion of the heat that is added to the block whose temperature is raised.

4. Carnot cycles

The operation last described, in which the working gas absorbs heat at lower temperatures and absorbs work, with a consequent development of both in the form of heat at the higher temperatures, is roughly analogous to the operation of a freight elevator employed to transport a barrel of flour from one floor of a warehouse to a higher floor, the elevator being thereupon returned to its initial position. For, in this operation, the elevator absorbs potential energy at a lower level and absorbs work, with a consequent development of both in the form of potential energy at the higher level. The analogy would be more complete if the transfers of heat in the thermodynamic operation were made at constant temperatures, which would then correspond to the constant floor-levels of the working elevator.

In any one of the cyclical operations employed in the reversible equalization of the temperatures of two metal blocks, the change of the temperature of each block would be infinitesimal if the blocks were relatively very large. In such a case the transfers of heat to and from the working gas would be almost perfectly isothermal. But it will be more satisfactory to consider transfers made in wholly isothermal processes. For example, let the hot block be replaced by a mass of liquid wax at

its melting temperature τ_2, and the cold block by a mass of ice at its melting temperature $\tau_1 < \tau_2$.   Utilizing the same auxiliary mass of gas as before, reversible expansion of the gas in contact with the wax will cause the gas to absorb a quantity of heat Q_2 at the constant temperature τ_2.   Then, after adiabatic expansion to the temperature τ_1, compression of the gas in contact with the ice will cause the gas to develop the quantity of heat Q_1 at the constant temperature τ_1; whereupon adiabatic compression will restore the gas to its initial state.   The net result is that the gas absorbs the heat Q_2, and develops the heat Q_1 and the work W.   Therefore, by the first law of thermodynamics,
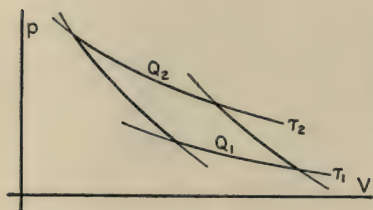
FIG. 8.

$$0 = - W + Q_2 - Q_1.$$

The freezing of some wax and the melting of some ice have been supplemented by a change of state consisting of an absorption of work.   The quantity of heat Q_2 has been absorbed at the temperature τ_2, and this quantity of heat has been converted into the work W developed and the heat Q_1 given out at the temperature τ_1.   This state of affairs is conveniently represented by the diagram of Fig. 9.

If the operation is reversed, the quantity of heat Q_1 is absorbed by the gas from the freezing water at the temperature τ_1,
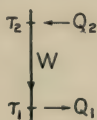
FIG. 9.
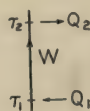
FIG. 10.

the work W is taken up, and the sum of the two is transferred to the melting wax at the temperature τ_2.   This is represented by the reversed diagram shown in Fig. 10.

Any reversible isothermal addition of heat to a body can be utilized as one of the steps of such a cycle of thermodynamic operations.   Even an isothermal transfer of heat that does not

alter the volume of the working body can be so utilized.   To
illustrate this, let the isothermal process be an isometric *
absorption of the quantity of heat Q_2 by a body composed of
coexistent masses of ice, liquid water, and water vapor at the
freezing temperature τ_2 of water.   The process will involve
fusion of some of the ice, and a slight increase of the mass of
the vapor — the specific volume of the liquid being less than
that of the ice.   Now, on adiabatic expansion, the working
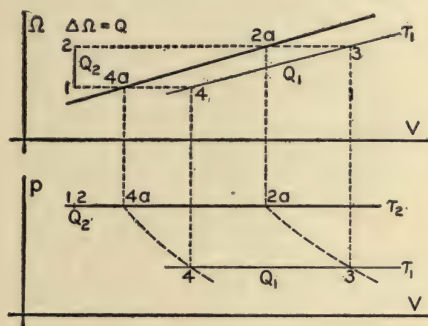
FIG. 11.†

body will first be converted into coexistent masses of ice and
vapor, without change of temperature ; and will then be brought
to a temperature $\tau_1 < \tau_2$.   On isothermal compression at this
temperature, until the path of compression meets the adiabatic
path passing through the initial state, a portion of the vapor
will condense (solidify) with development of a quantity of heat
Q_1.   The adiabatic compression concluding the cycle will raise
the temperature of the mass until liquefaction begins at τ_2, and
will then adiabatically and isothermally restore the body to its
initial state.   In this cyclical operation, the working body will
have absorbed the heat Q_2 at the temperature τ_2, will have de-
veloped the heat Q_1 at the temperature τ_1, and will have de-

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* Occurring at constant volume.

† A reader familiar with thermodynamics will recognize that the ordinate
Ω of the upper diagram, which is so chosen that on an isothermal path ab

$$Q_{ab} = \Omega_b - \Omega_a,$$
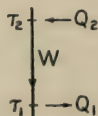
is the product ϑS of the absolute temperature ϑ and the entropy S of the
body.   For example, in this diagram,

$$Q_{12} = \vartheta_2(S_2 - S_1) = (\vartheta S)_2 - (\vartheta S)_1,$$
$$Q_{34} = \vartheta_1(S_4 - S_3) = (\vartheta S)_4 - (\vartheta S)_3.$$

veloped the quantity of work W represented by the enclosed area in the p, V-diagram of Fig. 11. The process, as before,

is represented by the diagram,

$$\tau_2 \mid \; -Q_2$$
$$\mid W$$
$$\tau_1 \mid \; -Q_1$$
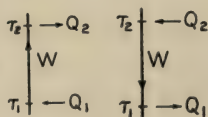
Any reversible cyclical thermodynamic operation composed of two isothermal processes and two adiabatic processes is termed a **Carnot cycle.** In any Carnot cycle, the quantity of heat $\pm\, Q_1$ absorbed by the working body at the lower temperature, the quantity of heat $\mp\, Q_2$ absorbed by the body at the higher temperature, and the quantity of work $\pm\, W$ absorbed, are connected by the relation

$$0 = W + Q_1 - Q_2 ;$$

and this relation can always be represented by one or the other
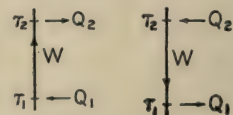
of the two diagrams

$$\tau_2 \mid \rightarrow Q_2 \quad \tau_2 \mid \; -Q_2$$
$$\mid W \qquad \mid W$$
$$\tau_1 \mid \; -Q_1 \quad \tau_1 \mid \rightarrow Q_1$$

5. The operation of a freight elevator

In a Carnot cycle, the heat Q_1 absorbed at the temperature τ_1, and the work W absorbed by the working body, may be regarded as having been transformed into the heat Q_2 developed at the temperature τ_2. In a similar way, the potential energy Q_1 added to a freight elevator with a barrel of flour at the height τ_1, and the work W absorbed by the elevator in transporting the barrel to the height τ_2 and returning the empty elevator to its initial position, are regarded as having been transformed into the potential energy Q_2 developed by the

elevator at the height τ_2.   The diagrams,

$$\tau_2 \mid \rightarrow Q_2 \quad \tau_2 \mid \; -Q_2$$
$$\mid W \qquad \mid W$$
$$\tau_1 \mid \; -Q_1 \quad \tau_1 \mid \rightarrow Q_1$$

employed to represent the operation of the Carnot cycle, repre-

sent the action of the elevator in transporting a barrel of flour from one floor of a warehouse to another.*

In view of this analogy, we shall undertake to examine how any given reversible positive or negative addition of potential energy to any elevator can be expressed by means of quantities determined by the state of the elevator; and thereupon we shall seek to determine whether any given reversible positive or negative addition of heat to any body can, in the same way, be expressed by means of quantities determined by the state of the body.

In the thermodynamic problem, the quantities that may be supposed to be given are: an arbitrary scale of temperatures τ, the quantities of heat Q_1, Q_2 transferred to and from the working body traversing any Carnot cycle, and the work W of the cycle. In the analogous problem of the elevator, it shall be supposed that the height of the elevator is determined with reference to an irregular scale of **heights** τ chalked off in the elevator shaft, and that the quantities of potential energy Q_1, Q_2 transferred to and from the elevator in any of its cyclical operations, and the work W of the cycle, are given. It is required that any given reversible transfer Q_{ab} of potential energy to or from the elevator shall be analytically expressed by means of quantities that are shown to be determined by the state of the elevator, and to be determinable from the given data.

It is obvious that the quantity of potential energy Q_{ab} transferred in a change of state of the elevator from the state a to the state b is not equal to the concurrent change of a quantity determined by the state of the elevator. For the value of Q_{ab} depends on the path ab; wherefore Q_{ab} is certainly not a differentiable function of quantities determined by the state of the elevator. Yet the differential of the transfer of potential energy can be given a definite meaning. Let W, Q be the work and potential energy absorbed by the elevator in any reversible change of state beginning with the state of reference † in which

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* The analogy between a Carnot cycle and the cyclical operation of an elevator is, however, not complete. Transfer of heat to or from a body, at a constant temperature, involves in general a transfer of work; but transfer of potential energy to or from the elevator, at a constant height, involves no transfer of work. Again, an isothermal transfer of heat has a definite value in work-units; but the value of a transfer of potential energy at a constant height depends on the position of the level of reference, and this level may be chosen arbitrarily.

† This state might be that of the empty elevator at the level of the basement floor.

the assigned value of the energy E of the elevator is zero.   In this process,

$$E = W + Q.$$

Here the energy E appears as a function of the independent variables W, Q.   In consequence, at any point on any reversible path,

$$dE = dW + dQ,$$

where dQ is the differential of the independent continuous variable Q.

Now, instead of treating the perfectly definite dQ as an independent differential, it is desired to express it by means of quantities determined by the state of level and load of the elevator.   If ϑ is the level (expressed in units of equal length), and S is the load (the total weight of the elevator and its cargo), the differential dQ is so expressed in the formulation

$$dQ = \vartheta dS.$$

When the elevator passes, on any assigned path, from the state a to any other state b, the concurrent addition of potential energy to it is

$$Q_{ab} = \int_a^b \vartheta dS,$$

the integration being taken over any assigned path of integration

$$\phi(\vartheta, S) = 0.$$

In particular, when the elevator passes at the constant level ϑ from the state α to the state β, the addition of potential energy is

$$Q_{\alpha\beta} = \vartheta(S_\beta - S_\alpha).$$

It will be noted that

$$E = \vartheta S,$$

wherein the energy appears as a function of independent variables ϑ, S that are determined by the state of the elevator; and that the independent differential dQ has been replaced by the *inexact* differential expression

$$\vartheta dS$$

in these variables.

But the relation

$$dQ = \vartheta d\mathrm{S}$$

is of no use to us until it is shown that this relation is satisfied by quantities ϑ,S that are determined by the state of the elevator and can be found from the given data. For our knowledge is supposed to be limited by the given data. From the given data it must be shown that reversible transfers of potential energy to or from the elevator can be expressed by means of determinable quantities ϑ,S determined by the state of the elevator. When this is accomplished, our problem is clear. It is to establish whether the positive or negative transfers of heat to a body in any reversible change of its thermodynamic state can be expressed, in the way in which transfers of potential energy to the elevator are expressed, by means of a determinate 'thermal level' ϑ and a determinate 'thermal load' S of the body. For the solution of this problem, it is necessary to show that the argument applicable to the operation of the elevator can be applied, without ambiguity or contradiction, to the analogous behavior of a body undergoing reversible changes of thermodynamic state.

6. The thermal level of a body

1. *The Initial Definition*

The first step in the execution of the programme just outlined is to determine the numerical value of the level ϑ corresponding to any given height τ of a given elevator,—to replace the irregular scale of heights τ by a scale of levels in which the unit difference of level is a constant length.

According to the formulation $dQ = \vartheta d\mathrm{S}$ that we seek to establish, when the elevator executes a cyclical operation of the Carnot type, transporting a load-increment $\mathrm{S}_\beta - \mathrm{S}_\alpha$ from the level ϑ_i to the level $\vartheta_j > \vartheta_i$, it absorbs at ϑ_j the potential energy

$$- Q_j = \vartheta_j(\mathrm{S}_\alpha - \mathrm{S}_\beta),$$

and it absorbs at ϑ_i the potential energy

$$Q_i = \vartheta_i(\mathrm{S}_\beta - \mathrm{S}_\alpha).$$

Since the energy of the elevator is not altered in the operation,

we have

$$0 = \Delta E$$
$$= W + Q_i - Q_j,$$
$$W = Q_j - Q_i$$

(1) $$= (\vartheta_j - \vartheta_i)(S_\beta - S_a).$$

When the elevator executes a succession of such cyclical operations transporting the load-increment $S_\beta - S_a$ from height to height, and each cycle absorbs the same quantity of work W, the first cycle absorbs the potential energy

$$Q_1 = \vartheta_1(S_\beta - S_a)$$

at the initial height τ_1, and develops the potential energy

$$Q_2 = \vartheta_2(S_\beta - S_a)$$

at the second height τ_2; the second cycle absorbs the potential energy Q_2 at τ_2, and develops the potential energy

$$Q_3 = \vartheta_3(S_\beta - S_a)$$

at the third height τ_3; and so on. In any such succession of cycles, the potential energy developed at a height τ_m in any one of the cycles is equal to the potential energy absorbed at τ_m in the succeeding cycle. Such a succession of 'equal-work cycles' shall be termed a **series** of cycles. In each cycle of such a series the quantities W and $S_\beta - S_a$ are constant; wherefore, by (1), the level-increments are the same for all. In accordance with this state of affairs, we begin with the definition:

DEF. The change of **level** $\vartheta_n - \vartheta$ corresponding to any given change of height $\tau_n - \tau$ of an elevator is the number of cycles in any 'series' of cycles between the two heights.

In applying this definition, the *unit* difference of level shall be arbitrarily fixed by assigning a fixed number of cycles to a series between two given heights.

In the thermodynamic problem, following the same procedure, we begin with the definition:

DEF. The change of **thermal level** $\vartheta_n - \vartheta$ corresponding to any given change of temperature $\tau_n - \tau$ of a body is the number of Carnot cycles in any 'series' of such cycles between the two temperatures.

By a 'series' of Carnot cycles is meant a succession of 'equal-work cycles,' in which the quantity of heat developed at a temperature τ_m in any one of the cycles is equal to the quantity of heat absorbed at τ_m in the succeeding cycle. And here, as in the elevator problem, the *unit* difference of thermal level shall be arbitrarily fixed by assigning a fixed number of cycles to a series between two given temperatures.

2. *The Fundamental Principle*

It must now be shown whether the foregoing definitions define determinate quantities. In the elevator problem it must be shown whether the number of cycles in any series of cycles between two given heights is determined by these heights; in the thermodynamic problem it must be shown whether the number of Carnot cycles in any series of such cycles between two given temperatures is determined solely by these temperatures.

In the elevator problem the governing consideration is the principle that: *A development of potential energy at constant height cannot supplement an absorption of work.* If this principle were not true, it would be possible to gain work through pushing a weight about at a constant height. In a cyclical operation of the elevator, work can be gained only when a weight is transferred *from* some floor of the warehouse and *to* a lower floor. The concurrent work-absorption of the mechanism controlling the elevator is then supplemented by the process occurring at the one floor, *together* with the process occurring at the other floor. A development of potential energy at a given floor cannot alone supplement an absorption of work.

In the thermodynamic problem the corresponding principle is that : *An isothermal development of heat, or a cooling of a body having a uniform temperature, cannot supplement an absorption of work.* It has already been noted that contiguous bodies having different temperatures spontaneously acquire a common intermediate temperature ; and that this spontaneous process, like all others, can be made to supplement an absorption of work. When the bodies have the same temperature, no spontaneous temperature equalization is possible ; and, in consequence, no work can be gained from their thermal action on each other. If this were not so, an absorption of work could be supplemented by a cooling of a body of uniform temperature. It would be possible to construct a motor that

should function at the expense of a cooling of the atmosphere
or of the sea.

3. *The Theorem of Carnot*

An immediate consequence of the principle that a develop-
ment of potential energy at a constant height cannot supplement
an absorption of work is the theorem that the work
$W[Q, \tau_n - \tau]$ absorbed in a cycle in which an elevator func-
tions between any two heights τ and $\tau_n > \tau$, and in which a
given quantity of potential energy Q is absorbed at τ, is inde-
pendent of the elevator and of the nature of the changes of
state involved.

To prove this, consider two such cycles, one absorbing Q with
a barrel of flour and one absorbing Q with a barrel of pork ;
or one conducted with the elevator A
and one with the elevator B. Suppose
the two cycles to absorb *different* quan-
tities of work, W and W'. On revers-
ing the operation of the cycle absorb-
ing $W' > W$, the two cycles can be coupled as represented by
the diagram. In each cyclical operation, the change of the
energy of the elevator employed is zero,
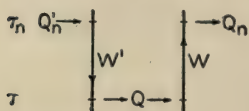
$$Q'_n - Q - W' = 0$$
$$- Q_n + Q + W = 0;$$

whence, by addition,

$$Q'_n - Q_n = W' - W.$$

We find, that is to say, that an absorption of the work $W' - W$
is supplemented by a development of the potential energy
$Q'_n - Q$ at the constant height τ_n. This being inadmissible,
we have

$$W = W';$$

which was to be proved.

An extension of the conclusion just established is the theorem
that a cycle operating between the given heights τ, τ_n, and hav-
ing a k-fold absorption of potential energy at τ, has a k-fold
work-absorption. In the notation employed above,

$$W[kQ, \tau_n - \tau] = k \cdot W[Q, \tau_n - \tau].$$

To demonstrate this theorem, consider a cycle working be-
tween τ and τ_n, absorbing the potential energy Q at τ, and ab-

sorbing the work W. And suppose that a second cycle, working between the same heights and absorbing kQ at τ, absorbs the work $W' + kW$. The latter cycle, when its operation is reversed, may be coupled with k of the former cycles, as represented by the diagram. (This will be the arrangement if $W' > kW$. If $W' < kW$, all the cycles should be reversed). The cyclical change of the energy of each elevator being zero,
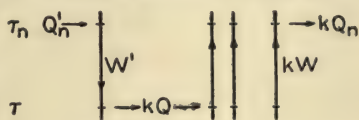
$$Q'_n - kQ - W' = 0$$
$$- kQ_n + kQ + kW = 0 ;$$

whence, by addition,

$$Q'_n - kQ_n = W' - kW.$$

We find that an absorption of the work $W' - kW$ is supplemented by a development of the potential energy $Q'_n - kQ_n$ at the constant height τ_n. This being inadmissible, we have

$$W' = kW ;$$

which was to be proved. The argument here is identical with that given in connection with the first diagram.

Since, now, a cycle operating between given heights τ, τ_n and having a k-fold absorption of potential energy Q has a k-fold work-absorption, irrespective of the elevator and of the nature of the changes of state involved, it appears that the ratio

$$\frac{Q}{W[Q, \tau_n - \tau]}$$

is determined by the heights τ, τ_n alone. From

(1) $$\frac{Q}{W} = f(\tau, \tau_n),$$

by substituting $W = Q_n - Q$, we find

(2) $$\frac{Q_n}{Q} = \frac{f + 1}{f} ;$$

and, by multiplying (1) and (2),

$$(3) \qquad\qquad \frac{Q_n}{W} = f + 1.$$

It thus appears that the ratios of the three quantities Q, Q_n, W are determined by the heights τ, τ_n alone. This theorem is a consequence of the fundamental principle that a development of potential energy at constant height cannot supplement an absorption of work.

———

We now proceed to develop the corresponding theorem relating to Carnot cycles of thermodynamic operations. From the fundamental principle that an isothermal development of heat cannot supplement an absorption of work, it follows that the work $W[Q, \tau_n - \tau]$ of a Carnot cycle operating between any two temperatures τ, τ_n, and in which a given quantity of heat Q is absorbed at τ, is independent of the working body and of the nature of the changes of state involved.

To prove this, consider two such cycles, these cycles involving either the same or different operations with the same working body (which may, for example, be taken initially at different states), or involving different working bodies. Suppose the two cycles to absorb *different* quantities of work, W and W'.
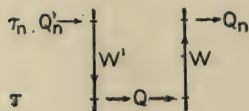
On reversing the cycle absorbing $W' > W$, the two cycles can be coupled as represented by the diagram. In each cyclical operation, the change of the energy of the working body is zero,

$$Q'_n - Q - W' = 0$$

$$- Q_n + Q + W = 0 \,;$$

whence, by addition,

$$Q'_n - Q_n = W' - W.$$

We find that an absorption of the work $W' - W$ is supplemented by a development of the heat $Q'_n - Q_n$ at the constant temperature τ_n. This being inadmissible, we have

$$W' = W \,;$$

which was to be proved.

An extension of this conclusion is the theorem that a Carnot cycle operating between the given temperatures τ, τ_n, and having a k-fold absorption of heat at τ, has a k-fold work-absorption,

$$W[kQ, \tau_n - \tau] = k . W[Q, \tau_n - \tau].$$

To show this, consider a cycle working between τ and τ_n, absorbing the heat Q at τ, and absorbing the work W. And suppose that a second cycle, working between the same temperatures and absorbing kQ at τ, absorbs the work $W' \neq kW$. The latter cycle, when its operation is reversed, may be coupled with k of the former cycles, as represented by the diagram. (This will be the arrangement if $W' > kW$. If $W' < kW$, all the cycles should be reversed.) The cyclical change of the energy of each working body being zero,
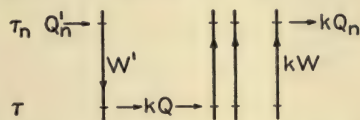
$$Q'_n - kQ - W' = 0$$

$$- kQ_n + kQ + kW = 0;$$

whence, by addition,

$$Q'_n - kQ_n = W' - kW.$$

We find that an absorption of the work $W' - kW$ is supplemented by a development of the heat $Q'_n - kQ_n$ at the constant temperature τ_n. This being inadmissible, we have

$$W' = kW;$$

which was to be proved.

Since, now, a Carnot cycle operating between given temperatures τ, τ_n and having a k-fold absorption of heat Q has a k-fold work-absorption, irrespective of the working body and of the nature of the changes of thermodynamic state involved, it appears that the ratio

$$\frac{Q}{W[Q, \tau_n - \tau]}$$

is determined by the temperatures τ, τ_n alone. From

$$\frac{Q}{W} = f(\tau, \tau_n),$$

by substituting $W = Q_n - Q$, we find

$$\frac{Q_n}{Q} = \frac{f+1}{f}, \qquad \frac{Q_n}{W} = f + 1.$$

It thus appears that the ratios of the three quantities Q, Q_n, W are determined by the temperatures τ, τ_n alone. This is the **theorem of Carnot.** It is a consequence of the fundamental principle that an isothermal development of heat cannot supplement an absorption of work.

4. *Changes of Thermal Level*

We are now in position to establish the validity of the initial definition of the present theory (cf. p. 44):

DEF. The change of **level** $\vartheta_n - \vartheta$ corresponding to any given change of height $\tau_n - \tau$ of an elevator is the number of cycles in any 'series' of cycles between the two heights.

In applying this definition, the *unit* difference of level is to be fixed by assigning a fixed number of cycles to the series between two given heights. It must be shown that, when the unit difference of level is so fixed, the definition defines a quantity that is independent of the elevator and of the nature of the changes of state involved in the series of cycles.

The problem reduces to the question: If each cycle of some one series absorbs the work W, and each cycle of some other series absorbs the work W'; and if the initial cycle of each series operates between any two fixed heights τ_1, τ_2; will the successive cycles of each series involve transfers of potential energy at the *same* heights, $\tau_1, \tau_2, \tau_3, \tau_4, \cdots$? If they will do so, it will be possible to determine the unit difference of level in the way prescribed; and the change of level corresponding to a given change of height will thereupon be determined by the terminal heights.

Let Q_1, and $Q_1' = kQ_1$, be the quantities of potential energy absorbed at τ_1 in the two series. By the theorem corresponding to Carnot's theorem, we shall have

$$W' = kW$$
$$Q_2' = kQ_2.$$

In the second cycles of the series, Q_2 and Q_2' are absorbed, Q_3

and Q_3' are developed, and we have

$$Q_3 = Q_2 + W$$
$$Q_3' = Q_2' + W'$$
$$= k(Q_2 + W)$$
$$= kQ_3.$$

In general, we find that,

$$Q_1' = kQ_1, \quad Q_2' = kQ_2, \quad Q_3' = kQ_3, \quad \text{etc.}$$

It follows that,

$$f(\tau_1, \tau_2) = \frac{Q_1}{W} = \frac{kQ_1}{kW} = \frac{Q_1'}{W'}$$

$$f(\tau_2, \tau_3) = \frac{Q_2}{W} = \frac{kQ_2}{kW} = \frac{Q_2'}{W'}$$

$$f(\tau_3, \tau_4) = \frac{Q_3}{W} = \frac{kQ_3}{kW} = \frac{Q_3'}{W'}$$

and so on. That is to say, the heights τ_n determined by the ratios Q_n'/W' are identical with those determined by the ratios Q_n/W. In each series the transfers of potential energy occur at the same heights: the definition of the change of level $\vartheta_n - \vartheta$ defines a quantity that depends only on the heights τ, τ_n.

The validity of the definition of changes of thermal level is to be established in the same way. The definition is:

DEF. The change of **thermal level** $\vartheta_n - \vartheta$ corresponding to any change of temperature $\tau_n - \tau$ of a body is the number of Carnot cycles in any 'series' of such cycles between the two temperatures.

And here, as in the elevator problem, the *unit* difference of thermal level is to be fixed by assigning a fixed number of cycles to the series between two given temperatures. It must be shown that, when the unit difference of thermal level is so fixed, the definition defines a quantity that is independent of the working body and of the nature of the changes of state involved in the series of cycles. The problem reduces to the question: If each cycle of some one series absorbs the work W,

and each cycle of some other series absorbs the work W'; and if the initial cycle of each series operates between any two fixed temperatures τ_1, τ_2; will the successive cycles of each series involve transfers of heat at the *same* temperatures, $\tau_1, \tau_2, \tau_3, \tau_4, \cdots$? If they will do so, it will be possible to determine the unit difference of thermal level in the way prescribed; and the change of thermal level corresponding to a given change of temperature will thereupon be determined by the terminal temperatures.

Let Q_1, and $Q_1' = kQ_1$, be the quantities of heat absorbed at τ_1 in the two series. By Carnot's theorem, we shall have

$$W' = kW$$

$$Q_2' = kQ_2.$$

In the second cycles of the series, Q_2 and Q_2' are absorbed, Q_3 and Q_3' are developed, and we have

$$Q_3 = Q_2 + W$$

$$Q_3' = Q_2' + W'$$

$$= k(Q_2 + W)$$

$$= kQ_3.$$

In general we find that,

$$Q_1' = kQ_1, \quad Q_2' = kQ_2, \quad Q_3' = kQ_3, \quad \text{etc.}$$

It follows that,

$$f(\tau_1, \tau_2) = \frac{Q_1}{W} = \frac{kQ_1}{kW} = \frac{Q_1'}{W'}$$

$$f(\tau_2, \tau_3) = \frac{Q_2}{W} = \frac{kQ_2}{kW} = \frac{Q_2'}{W'}$$

$$f(\tau_3, \tau_4) = \frac{Q_3}{W} = \frac{kQ_3}{kW} = \frac{Q_3'}{W'}$$

and so on. That is to say, the temperatures τ_n determined by the ratios Q_n'/W' are identical with those determined by the ratios Q_n/W. In each series of cycles the transfers of heat occur at the same temperatures: the definition of the change of 'thermal level' $\vartheta_n - \vartheta$ defines a quantity that depends only on the temperatures τ, τ_n.

5. *The Thermal Level*

In the elevator problem, we now have a means by which any prescribed change of the level of a given elevator can be realized. In particular, any *unit* change of this level can be realized. But, in the level unit chosen, the value of the level ϑ corresponding to any assigned height τ is yet indeterminate, — the scale of levels contains as yet an arbitrary additive constant.

Yet the value of ϑ can be determined from the available data. Our undertaking, it will be recalled, is to establish the existence of quantities ϑ, S determined by the state of the elevator and such that the differential expression ϑdS shall be equal to the independent differential dQ,

$$dQ = \vartheta dS.$$

If such quantities exist, the potential energy absorbed by the elevator in any change of state $\alpha\beta$ occurring at the constant height τ is

(1)
$$Q_{\alpha\beta} = \vartheta(S_{\beta} - S_{\alpha}).$$

Again, on any path for which $dQ = 0$, and accordingly $dE = dW$, we have $dS = 0$. So, on the path subject to the condition $dQ = 0$ and passing through the state α (respectively the state β), we find $S = S_{\alpha}$ (respectively $S = S_{\beta}$). Consequently, on paths at the constant heights τ, τ_n intercepting these paths S_{α}, S_{β}, we have

$$Q_n = \vartheta_n(S_{\beta} - S_{\alpha})$$
$$Q_{\alpha\beta} = \vartheta(S_{\beta} - S_{\alpha}).$$

Further, by the energy law,

$$W[Q_{\alpha\beta}, \tau_n - \tau] = Q_n - Q_{\alpha\beta}.$$

So the quantity ϑ that it is sought to establish must satisfy the relation

$$W[Q_{\alpha\beta}, \tau_n - \tau] = (\vartheta_n - \vartheta)(S_{\beta} - S_{\alpha});$$

and, in particular, with reference to a cycle operating through the now realizable interval of height corresponding to $\vartheta_n - \vartheta = 1$ (which shall be termed a ' one-degree cycle '), it must satisfy

(2)
$$W[Q_{\alpha\beta}, 1°] = S_{\beta} - S_{\alpha}.$$

Since, now, the quantity ϑ must satisfy both (1) and (2), which are

$$Q_{\alpha\beta} = \vartheta(S_\beta - S_\alpha)$$
$$W[Q_{\alpha\beta}, 1°] = S_\beta - S_\alpha,$$

it appears that it must satisfy the relation

$$\vartheta = \frac{Q_{\alpha\beta}}{W[Q_{\alpha\beta}, 1°]}.$$

According to this equation, the level ϑ corresponding to any accessible height τ is determined by a ratio that, by the theorem analogous to the theorem of Carnot, is uniquely determined by the height τ.

Thus the level ϑ is determined, not by its excess above an arbitrary value assigned to some height of reference, but so that it shall satisfy the equation

$$Q_{\alpha\beta} = \vartheta \cdot W[Q_{\alpha\beta}, 1°]$$
$$= \vartheta(S_\beta - S_\alpha).$$

It is determined so that any quantity of potential energy $Q_{\alpha\beta}$ transferred at the level ϑ may be regarded as producible by transport of a weight $S_\beta - S_\alpha$ to the level ϑ from the level from which the given value of $Q_{\alpha\beta}$ is actually reckoned.

In the thermodynamic problem, we now have a means by which any prescribed change of the thermal level of any given body can be realized. In particular, any *unit* change of this level can be realized. But, in the level unit chosen, the value of the thermal level ϑ corresponding to any assigned temperature τ is yet indeterminate, — the scale of thermal levels contains as yet an arbitrary additive constant.

Yet the value of ϑ can be determined from the available data. It will be recalled that, in pursuing the analogy between the thermodynamic behavior of a body and the operation of a freight elevator, it is sought to establish the existence of quantities ϑ, S determined by the thermodynamic state of the body and such that the differential expression ϑdS shall be equal to the independent heat-differential dQ,

$$dQ = \vartheta dS.$$

If such quantities exist, the quantity of heat absorbed by the body in any reversible isothermal change of state $\alpha\beta$ is

$$(1) \qquad\qquad Q_{\alpha\beta} = \vartheta(S_\beta - S_\alpha).$$

In this proposed relation, the quantity of heat $Q_{\alpha\beta}$ appears as the concurrent change of the quantity ϑS, and so as independent of the isothermal path $\alpha\beta$. The relation is inadmissible unless it can be shown that $Q_{\alpha\beta}$ is independent of the path $\alpha\beta$. For, a given reversible isothermal change of the thermodynamic state of a body may, in general, occur on different paths. Consider, for example, the isothermal dilution of an aqueous solution of cane sugar by an added mass of water. This process may be conducted reversibly by reversible evaporation of the water, expansion of the resulting vapor, and condensation of this vapor upon the solution. It can be reversibly conducted on a different path, in consequence of the fact that the two liquids can be separated by a piston permeable only by the water. When so separated, the tendency of the liquids to mix — the 'affinity' between the sugar and the water — can be counterbalanced by a force applied to the piston. On infinitesimally relaxing this force, a reversible isothermal dilution of the solution is effected.

Consider any two reversible isothermal paths between the states α, β of any given body. The change of the energy of the body is the same along each path,

$$E_\beta - E_\alpha = W_{\alpha\beta} + Q_{\alpha\beta}$$
$$= W'_{\alpha\beta} + Q'_{\alpha\beta}.$$

Further, the quantities of work $W_{\alpha\beta}$ and $W'_{\alpha\beta}$ are equal; for, if they were not, an isothermal cycle, forward on one path and back on the other, would give rise to an absorption of work supplemented by an isothermal development of heat, in conflict with the fundamental principle from which the theorem of Carnot is deduced. Consequently,

$$Q_{\alpha\beta} = Q'_{\alpha\beta} ;$$

the heat transfer $Q_{\alpha\beta}$ is independent of the isothermal path $\alpha\beta$.[*]

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[*] Another form of this argument is as follows. Consider the body to traverse two Carnot cycles, between any two temperatures τ and $\tau_n > \tau$, ab-

Now, any reversible adiabatic change of the thermodynamic state of a body is subject to the condition $dQ = 0$; wherefore the relation,

$$dQ = \vartheta dS,$$

that ϑ, S are required to satisfy, requires that on any adiabatic path $dS = 0$. So, on an adiabatic passing through the state α of the body (respectively the state β), we find $S = S_a$ (respectively $S = S_\beta$). Consequently, on isotherms τ, τ_n intercepting these adiabatics S_a, S_β, we have

$$Q_n = \vartheta_n(S_\beta - S_a)$$
$$Q_{a\beta} = \vartheta(S_\beta - S_a).$$

Further, by the first law of thermodynamics,

$$W[Q_{a\beta}, \tau_n - \tau] = Q_n - Q_{a\beta}.$$

So the thermal level ϑ that it is sought to establish must satisfy the relation

$$W[Q_{a\beta}, \tau_n - \tau] = (\vartheta_n - \vartheta)(S_\beta - S_a);$$

and, in particular, with reference to a cycle operating through the now realizable temperature interval corresponding to $\vartheta_n - \vartheta = 1$ (which shall be termed a 'one-degree cycle'), it must satisfy

(2) $$W[Q_{a\beta}, 1^\circ] = S_\beta - S_a.$$

Since, now, the thermal level ϑ must satisfy both (1) and (2), which are

$$Q_{a\beta} = \vartheta(S_\beta - S_a)$$
$$W[Q_{a\beta}, 1^\circ] = S_\beta - S_a,$$

it appears that it must satisfy the relation

$$\vartheta = \frac{Q_{a\beta}}{W[Q_{a\beta}, 1^\circ]}.$$

---

sorbing — Q_n at τ_n, and absorbing $Q_{a\beta}, Q'_{a\beta}$ on different paths $a\beta$ at τ. By the theorem of Carnot, the ratios

$$\frac{Q_n}{Q_{a\beta}}, \qquad \frac{Q_n}{Q'_{a\beta}}$$

are equal to the same function of τ, τ_n. It follows that $Q_{a\beta} = Q'_{a\beta}$.

According to this equation, the thermal level ϑ corresponding to any accessible temperature τ is determined by a ratio that, by the theorem of Carnot, is uniquely determined by the temperature τ.

Thus the thermal level ϑ is determined, not by its excess above an arbitrary value assigned to some temperature of reference, but so that it shall satisfy the equation

$$Q_{\alpha\beta} = \vartheta \cdot W[Q_{\alpha\beta}, 1°].$$

It is determined so that any quantity of heat $Q_{\alpha\beta}$ added to a body at the temperature τ has the value that it *would have if it were produced* from the work absorbed in a 'series' of one-degree cycles beginning at a hypothetical thermal level $\vartheta = 0$, at which level an isothermal operation absorbs no heat. The *existence* of such a level does not enter into the argument at all.

The analogy of this formulation with the formulation of the level of an elevator whose zero level is inaccessible is obvious. The possibility of the formulation is a consequence of the theorem of Carnot.

7. The thermal load of a body

Now that a means has been found for the determination of the levels ϑ corresponding to all the accessible heights of an elevator, it is sought to establish that the relation

$$dQ = \vartheta dS$$

is satisfied by the differential of a quantity S that is determined by the state of the elevator and can be found from the given data. That the expression

$$\frac{dQ}{\vartheta}$$

is equal to the differential of a quantity that is determined by the state of the elevator will be established if it is established that

$$S\frac{dQ}{\vartheta} = 0,$$

where the summation is extended over any reversible closed path of change of the state of the elevator.

The level ϑ of the elevator absorbing the potential energy $Q_{\alpha\beta}$ at the height τ is uniquely defined by the relation

$$\vartheta = \frac{Q_{\alpha\beta}}{W[Q_{\alpha\beta},1°]}.$$

Let Q_n be the potential energy absorbed at any height $\tau_n > \tau$ on any path intercepted by the paths S_α, S_β. The level ϑ_n corresponding to the height τ_n is determined by

$$\vartheta_n = \frac{Q_n}{W[Q_n,1°]}.$$

Since 'one-degree cycles' operating between given paths, for each of which $dQ = 0$, absorb equal quantities of work, we have

$$W[Q_{\alpha\beta},1°] = W[Q_n,1°].$$

So, with reference to any cycle in which the elevator absorbs the potential energy $Q_{\alpha\beta}$ at τ, and absorbs $-Q_n$ at τ_n, we shall have

$$\vartheta = \frac{Q_{\alpha\beta}}{W}, \qquad \vartheta_n = \frac{-Q_n}{W};$$

whence, writing Q for $Q_{\alpha\beta}$,

$$\frac{Q}{\vartheta} + \frac{Q_n}{\vartheta_n} = 0.$$

Any reversible closed path of change of the state of level and load of the elevator can be approximated by a broken path composed of successive paths belonging to a succession of cycles of the Carnot type. If, in any one of these cycles, δQ be the potential energy absorbed at the lesser height τ, and $-\delta Q_n$ be that absorbed at the greater height τ_n, we shall have

$$\frac{\delta Q}{\vartheta} + \frac{\delta Q_n}{\vartheta_n} = 0;$$

wherefore, on summing over the whole group of cycles,

$$\Sigma\left(\frac{\delta Q}{\vartheta} + \frac{\delta Q_n}{\vartheta_n}\right) = 0;$$

or, considering the summation to be extended over the broken cyclical path,

$$\sum \frac{\delta Q}{\vartheta} = 0.$$

If, now, it may be assumed that the quantity of potential energy absorbed on the initially given path is the limit of the sum of the quantities absorbed on the successive portions of the broken path for which $d\tau = 0$, we shall have

$$S \frac{dQ}{\vartheta} = 0,$$

the summation being taken over the initially closed path. It follows that the expression dQ/ϑ is equal to the differential of a quantity S determined by the state of the elevator,

$$\frac{dQ}{\vartheta} = dS.$$

It is accordingly shown that the relation

$$dQ = \vartheta dS$$

is satisfied by the differential of a quantity S that is determined by the state of the elevator, and that, by means of the relation

$$S = S_0 \frac{dQ}{\vartheta} + S_0,$$

can be found from the given data. The quantity S is the 'load' of the elevator. Being defined by its differential, the load contains an arbitrary additive constant. This constant S_0 is the arbitrarily assigned value of the load when the elevator is in an arbitrarily chosen state of reference.

We now return to the thermodynamic problem. Now that a means has been found for the determination of the thermal levels ϑ corresponding to all the accessible temperatures of a body, it is sought to establish that the relation

$$dQ = \vartheta dS$$

is satisfied by the differential of a quantity S that is determined by the thermodynamic state of the body and can be found from the given data. That the expression

$$\frac{dQ}{\vartheta}$$

is equal to the differential of a quantity that is determined by the state of the body will be established if it is established that

$$S \frac{dQ}{\vartheta} = o,$$

where the summation is extended over any reversible closed path of change of the thermodynamic state of the body.

If this relation is obtainable, it must follow from the relation connecting the heat transfers of a Carnot cycle with the thermal levels at which these transfers are made. The thermal level ϑ of a body absorbing the heat $Q_{\alpha\beta}$ at the temperature τ is uniquely defined by the relation

$$\vartheta = \frac{Q_{\alpha\beta}}{W[Q_{\alpha\beta},1^\circ]}.$$

Let Q_n be the heat absorbed at any temperature $\tau_n > \tau$ on any isothermal path intercepted by any two adiabatic paths passing through the states α,β. The thermal level ϑ_n corresponding to the temperature τ_n is determined by

$$\vartheta_n = \frac{Q_n}{W[Q_n,1^\circ]}.$$

Since 'one-degree cycles' operating between given adiabatic paths absorb equal quantities of work, we have

$$W[Q_{\alpha\beta},1^\circ] = W[Q_n,1^\circ].$$

So, with reference to any cycle in which the body absorbs $Q_{\alpha\beta}$ at τ, and absorbs $-Q_n$ at τ_n, we shall have

$$\vartheta = \frac{Q_{\alpha\beta}}{W}, \quad \vartheta_n = \frac{-Q_n}{W};$$

whence, eliminating W,

$$\frac{Q_{\alpha\beta}}{\vartheta} + \frac{Q_n}{\vartheta_n} = 0.$$

It thus appears that, when Q is the heat absorbed at τ in *any* Carnot cycle operating between any two temperatures τ, τ_n, we have

$$\frac{Q}{\vartheta} + \frac{Q_n}{\vartheta_n} = 0.$$

If it be assumed that the path of any reversible change of the thermodynamic state of a body lies in the continuous field of a family of isothermal paths; and if it be assumed that the path lies also in the continuous field of a family of adiabatic
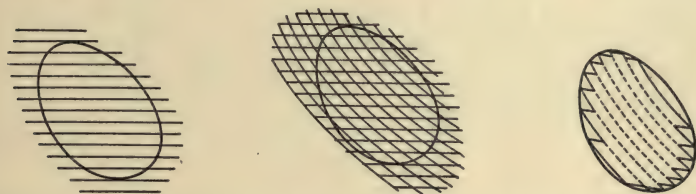
paths; it may be concluded that any reversible closed path can be approximated by a broken path composed of successive isothermal and adiabatic paths belonging to a succession of Carnot cycles.

If, in any one of these cycles, δQ be the heat absorbed at the lower temperature τ, and $-\delta Q_n$ be that absorbed at the higher temperature τ_n, we shall have

$$\frac{\delta Q}{\vartheta} + \frac{\delta Q_n}{\vartheta_n} = 0 ;$$

wherefore, on summing over the whole group of cycles,

$$\Sigma\left(\frac{\delta Q}{\vartheta} + \frac{\delta Q_n}{\vartheta_n}\right) = 0 ;$$

or, considering the summation to be extended over the broken cyclical path,

$$\Sigma \frac{\delta Q}{\vartheta} = 0.$$

If, now, it may be assumed that the heat absorbed on the initially given path is the limit of the sum of the quantities of heat absorbed on the successive isothermal portions of the broken path, we shall have

$$S \frac{dQ}{\vartheta} = 0,$$

the summation being taken over any reversible cyclical change of the thermodynamic state of any body. It follows that the expression dQ/ϑ is equal to the differential of a quantity S determined by the thermodynamic state of the body,

$$\frac{dQ}{\vartheta} = dS.$$

The quantity S is the 'thermal load' of the body. In any reversible change of the thermodynamic state of the body from any state a to any other state b, the concurrent change of the thermal load of the body is

$$S_b - S_a = S_a^b \frac{dQ}{\vartheta}.$$

The quantity S, being defined by its differential, contains an arbitrary additive constant. When the scale of thermal levels ϑ corresponding to the accessible temperatures τ of a given scale of temperatures is once established, the thermal load of the body is determined by the relation

$$S = S_0 \frac{dQ}{\vartheta} + S_0;$$

where the summation is taken over any *reversible* thermodynamic path from an arbitrarily chosen state of reference, in which state the thermal load has the arbitrarily assigned value S_0.

It is therefore established that the relation,

$$dQ = \vartheta dS,$$

suggested by the behavior of a freight elevator, *is* satisfied by the differential of a quantity S that is determined by the thermodynamic state of the body and can be found from the

given data.   This conclusion is the **second law of thermo-dynamics.**   It may be restated in the words :

When a body passes from any thermodynamic state a *to any other thermodynamic state* b *in a reversible thermodynamic operation, the quantity*

$$\underset{a}{\overset{b}{\mathrm{S}}}\ \frac{d\mathrm{Q}}{\vartheta}$$

is equal to the concurrent change of a quantity S, *which quantity is determined by the state of the body, has one value for each state, and contains an arbitrary additive constant.*

8. Reversible transfers of heat

The aim of the present chapter is to show that any reversible addition of heat Q_{ab} to a given body can be analytically expressed by means of quantities that are determined by the thermodynamic state of the body, and whose values can be found by experimental means.   This aim is attained in the formulation

$$Q_{ab} = \int_a^b \vartheta d\mathrm{S},$$

where the integration is taken over an assigned   path of integration

$$\phi(\vartheta, \mathrm{S}) = \mathrm{o}.$$

The formulation is a formulation of the second law of thermodynamics.   It represents an addition of heat to the body by means of the thermal level and thermal load of the body, in exactly the way in which additions of potential energy to an elevator are represented by means of the level and load of the elevator.

With reference to any reversible change *ab* of the thermodynamic state of a given body, the first law of thermodynamics

$$\mathrm{E}_b - \mathrm{E}_a = \mathrm{W}_{ab} + \mathrm{Q}_{ab},$$

and the second law of thermodynamics

$$Q_{ab} = \int_a^b \vartheta d\mathrm{S},$$

are together expressed by the equation

$$E_b - E_a = W_{ab} + \int_a^b \vartheta dS.$$

When the work W_{ab} is added to the body through the reversible action of a uniform and normally directed pressure p, we have

$$E_b - E_a = - \int_a^b pdV + \int_a^b \vartheta dS;$$

where V is the volume of the body, and the work-integral is taken over the path $\psi(p, V) = 0$ determined by the assigned path of integration $\phi(\vartheta, S) = 0$.

The scale of thermal levels ϑ, for the reason that ϑ is a measure of temperature and is independent of the specific properties of any thermometric body, is termed the scale of **absolute temperatures.** The thermal load S of any given body is termed the **entropy** of the body. In any actually occurring change ab of the thermodynamic state of the body, the concurrent change of the entropy of the body is the value of the sum

$$\overset{b}{\underset{a}{S}} \frac{dQ}{\vartheta},$$

taken over any *reversible* path between the end states a and b.

9. The theorem of Carnot

The equation

(1)
$$dQ = \vartheta dS$$

renders it possible to express the theorem of Carnot by means of the absolute temperatures at which the heat transfers occur in a Carnot cycle. In the foregoing, the theorem of Carnot has been expressed by the relations,

$$\frac{Q}{W} = f(\tau, \tau_n), \quad \frac{Q_n}{Q} = \frac{f+1}{f}, \quad \frac{Q_n}{W} = f + 1.$$

Now, from (1), we find

$$Q = \vartheta \cdot \Delta S$$
$$Q_n = \vartheta_n \cdot \Delta S;$$

whence, because of the first law of thermodynamics,

$$W = Q_n - Q$$
$$= (\vartheta_n - \vartheta) \cdot \Delta S.$$

These equations yield,

$$\frac{Q}{W} = \frac{\vartheta}{\vartheta_n - \vartheta}, \quad \frac{Q_n}{Q} = \frac{\vartheta_n}{\vartheta}, \quad \frac{Q_n}{W} = \frac{\vartheta_n}{\vartheta_n - \vartheta}.$$

From the last equation, which may be written

$$W = \frac{\vartheta_n - \vartheta}{\vartheta_n} Q_n,$$

it appears that, in the operation of the cycle, the fractional part

$$\frac{\vartheta_n - \vartheta}{\vartheta_n}$$

of the heat absorbed at τ_n is converted into work. This fraction is accordingly termed the 'efficiency' of the cycle. According to Carnot's theorem, the efficiency of a Carnot cycle depends on the temperatures between which the cycle operates, and is independent of the nature of the working body. The application of this observation to the reversible operation of an elevator is obvious.

10. Summary of Chapter III.

The Problem

In order to express the first law of thermodynamics,

$$E_b - E_a = M_{ab} + Q_{ab},$$

be means of quantities determined by the thermodynamic state of the body undergoing the change of state ab, it is necessary to express the terms M_{ab} and Q_{ab} by means of such quantities. With regard to a *reversible* path, the quantity M_{ab} is the *work* W_{ab} of forces supported by the body. The work of such a force is the product of the force into the effected displacement; and the force and the displacement are quantities that are determined by the state of the body. The work W_{ab} depends in general on the path; therefore the concurrent transfer of heat Q_{ab} depends on the path. It is required to show whether this

transfer of heat can be expressed by means of quantities determined by the thermodynamic state of the body.

A Mechanical Analogy

Any isothermal reversible transfer of heat to or from a body can be one step of a reversible cyclical operation — a Carnot cycle — in which the body traverses two isothermal and two adiabatic paths. In any Carnot cycle, the heat absorbed at the lower temperature and the absorbed work are together converted into the heat developed at the higher temperature. And the reverse.

In a similar way, any reversible transfer of potential energy to or from a freight elevator at a constant height can be one step of a reversible cyclical operation in which the elevator transports an increment of load between different heights. In this cycle, the potential energy absorbed at the lesser height and the absorbed work are together converted into the potential energy developed at the greater height. And the reverse.

Accordingly, the thermodynamic cycle and the mechanical cycle are analogous operations. In the case of the elevator, when the height and the transferred quantities of potential energy and of work are given, the transfers of potential energy can be analytically expressed by means of quantities that are determined by the state of the elevator, and whose values can be found by experimental means. For the independent differential dQ of the added potential energy is equal to the expression ϑdS, where the 'level' ϑ and 'load' S of the elevator are uniquely determined by the mechanical state of the elevator and can be found from the given data.

Can the analogous thermodynamic case be treated in the same way? When the temperatures and the transferred quantities of heat and of work are given, can the transfers of heat be expressed, in the way in which transfers of potential energy to or from the elevator are expressed, by means of a 'thermal level' and a 'thermal load' of the body? Is the relation

$$dQ = \vartheta dS$$

satisfied by a quantity ϑ and the differential of a quantity S, which quantities ϑ, S are uniquely determined by the thermodynamic state of the body and can be found from the given data? It must be shown whether the reasoning requisite to

establish this relation in the problem of the elevator will establish it in the thermodynamic problem.

The Thermal Level of a Body

The first step of the reasoning is to define the increment $\vartheta_n - \vartheta$ of thermal level, corresponding to any increment $\tau_n - \tau$ of temperature, by the number of Carnot cycles in any 'series' of such cycles between the two temperatures. When expressed in an arbitrarily chosen unit, is this defined change of level determined by τ, τ_n alone? From the principle that an isothermal development of heat cannot supplement an absorption of work, it follows that the work W absorbed in any Carnot cycle operating between τ, τ_n and absorbing a given quantity of heat Q at τ is determined by τ, τ_n; and it follows that any Carnot cycle operating between τ, τ_n and absorbing kQ at τ absorbs kW. Hence the theorem of Carnot, that the ratios $Q : Q_n : W$ depend on τ, τ_n alone. From the theorem of Carnot it follows that the change of thermal level $\vartheta_n - \vartheta$ is uniquely determined by τ, τ_n.

Thus is determined any prescribed change of the thermal level ϑ of a given body ; but not the value of ϑ corresponding to a given τ. If the relation

$$dQ = \vartheta dS$$

is satisfied by quantities ϑ, S determined by the state of the body, the level ϑ must satisfy

(1) $Q_{\alpha\beta} = \vartheta(S_\beta - S_\alpha)$.

This consequence requires $Q_{\alpha\beta}$ to be independent of the isothermal path $\alpha\beta$. That this requirement is fulfilled, follows from the principle that an isothermal development of heat cannot supplement an absorption of work. Further, on an adiabatic path S must satisfy $dS = 0$; wherefore in a Carnot cycle S must satisfy

(2) $W[Q_{\alpha\beta}, 1°] = S_\beta - S_\alpha$.

Since ϑ must satisfy both (1), (2), it must satisfy

$$\vartheta = Q_{\alpha\beta} / W[Q_{\alpha\beta}, 1°].$$

By Carnot's theorem, the thermal level ϑ defined by this equation is determined by τ alone.

The Thermal Load of a Body

It remains to establish whether the relation

$$dQ = \vartheta dS$$

is satisfied by the differential of a quantity S that is uniquely determined by the thermodynamic state of the body and can be found from the given data. In any Carnot cycle in which the body absorbs Q at τ and absorbs $- Q_n$ at τ_n, the thermal levels ϑ, ϑ_n are

$$\vartheta = \frac{Q}{W}, \qquad \vartheta_n = \frac{Q_n}{W};$$

whence

$$\frac{Q}{\vartheta} + \frac{Q_n}{\vartheta_n} = 0.$$

If any reversible closed path of change of the thermodynamic state of the body can be approximated by a succession of isothermal and adiabatic paths belonging to a succession of Carnot cycles; and if the quantity of heat absorbed on the closed path is the limit of the sum of the quantities of heat absorbed on the broken path; we shall have, summing over the closed path,

$$S\frac{dQ}{\vartheta} = 0.$$

Subject to the assumptions here made, it follows that dQ/ϑ is equal to the differential of a quantity S that is uniquely determined by the state of the body. This conclusion is the second law of thermodynamics.

Transfers of Heat

It thus appears that the thermodynamic state of a body uniquely determines quantities ϑ, S that can be found from the given data and are such that

$$dQ = \vartheta dS.$$

Accordingly, in the formulation

$$Q_{ab} = \int_{a}^{b} \vartheta dS,$$

any reversible transfer Q_{ab} of heat to or from the body, on any assigned path $\phi(\vartheta, S) = 0$, is represented by means of quantities determined by the thermodynamic state of the body. In consequence, in the equation

$$E_b - E_a = W_{ab} + \int_a^b \vartheta d\dot{S},$$

the first law of thermodynamics is expressed by means of quantities so determined. The 'thermal level' ϑ and the 'thermal load' S are termed the *absolute temperature* and the *entropy* of the body.

CHAPTER IV. The Absolute Temperature

1. The absolute temperature an integrating divisor

It shall now be shown how the absolute temperatures ϑ corresponding to the temperatures τ of a *given scale* of accessible temperatures can be expressed by means of τ. This can be done by expressing the definition of the absolute temperature by means of properties of a body that depend in a known way on the temperature τ of the body. For the definition of ϑ will then be expressed by means of functions of τ. We must begin, therefore, by expressing ϑ by means of thermodynamic properties of some body.

We shall seek to connect the absolute temperature ϑ with the temperatures τ of the scale of a constant pressure gas-thermometer. This variable τ is defined by means of a thermodynamic property of the thermometric gas. So the definition of ϑ must be expressed by means of thermodynamic properties of some aeriform body.

Let the thermometric body be a given mass of some substance whose liquid states exist only at very low temperatures. A given mass of hydrogen, or of nitrogen, or of air is such a body. And let it be supposed that the body selected is acted upon by no force other than a uniform and normally directed pressure. Over a wide range of accessible temperatures, the thermodynamic states of this body are aeriform states; and it is observed that these realizable aeriform states are uniquely determined by the volume v and the temperature τ of the body.

Within the region of the realizable aeriform states of the body, the absolute temperature ϑ of the body is continuously determined by the variable τ; and the entropy s of the body, being determined continuously and uniformly by the state, is so determined by the continuous variables v,τ. Now, any quantity that is continuously determined, within a given region, by one or by two independent variables that are continuous within the region can be expressed, with any desired accuracy, by a rational function of the variables, of a finite degree. Any empirical curve or surface, that is to say, can be represented by a differentiable function of the variables that determine it. Accordingly, within the region of the realizable aeriform states of the

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chosen thermometric body, the absolute temperature ϑ and the entropy s of the body can be considered to be differentiable functions

$$\vartheta = \vartheta(\tau), \quad s = s(v,\tau),$$

of the independent continuous variables v,τ.

Within this region, then, for the independent differential dQ of the preceding chapter we may write

$$dQ = \vartheta ds$$

$$= \vartheta \frac{\partial s}{\partial v}\, dv + \vartheta \frac{\partial s}{\partial \tau}\, d\tau$$

$$= c_\tau dv + c_v d\tau \; ;$$

where the coefficients c_τ, c_v are the functions

$$\vartheta \frac{\partial s}{\partial v}, \qquad \vartheta \frac{\partial s}{\partial \tau},$$

and the second member is an *inexact, linear, differential expression* in v,τ. We thus find

(1)
$$ds = \frac{c_\tau dv + c_v d\tau}{\vartheta} \; ;$$

an equation which asserts that, within the region of realizable aeriform states, the function $\vartheta(\tau)$ is an integrating divisor of the 'heat-differential'

$$c_\tau dv + c_v d\tau$$

of the body.*

2. The absolute temperature is uniquely defined

The equation (1) completely defines the absolute temperature $\vartheta(\tau)$. For when an integrating factor of a linear differential form is a function of one of the variables alone it is unique ; no other integrating factor is a function of this variable alone.

For the special case of two independent variables, this important theorem may be proved as follows. Let ϑ_1, ϑ_2 be any two integrating factors of the form

$$c_1 dx_1 + c_2 dx_2.$$

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* It must be remembered that this heat-differential is such only with reference to *reversible* paths.

We have

$$(2) \qquad \begin{cases} du_1 = \vartheta_1(c_1 dx_1 + c_2 dx_2) \\ du_2 = \vartheta_2(c_1 dx_1 + c_2 dx_2); \end{cases}$$

whence follows that

$$\begin{vmatrix} \dfrac{\partial u_1}{\partial x_1} & \dfrac{\partial u_1}{\partial x_2} \\ \dfrac{\partial u_2}{\partial x_1} & \dfrac{\partial u_2}{\partial x_2} \end{vmatrix} = \begin{vmatrix} \vartheta_1 c_1 & \vartheta_1 c_2 \\ \vartheta_2 c_1 & \vartheta_2 c_2 \end{vmatrix} = 0.$$

We therefore have

$$u_1 = f(u_2)$$
$$(3) \qquad du_1 = f' \cdot du_2;$$

where f', being a function of u_2, contains *both* variables x_1, x_2. Now, from the equations (2), by division,

$$du_1 = \frac{\vartheta_1}{\vartheta_2} du_2;$$

wherefore, on comparison with (3),

$$\frac{\vartheta_1}{\vartheta_2} = f'(u_2).$$

This equation shows that the ratio of any two integrating factors contains both of the variables. If, therefore, any integrating factor is a function of one of the variables alone, it is unique; every other integrating factor contains the other variable, and may contain both of the variables. The theorem can be proved in the same way for the case of n variables.

3. The differential equation for the absolute temperature

By means of the two laws of thermodynamics, the absolute temperature of our thermometric body is brought into connection with the energy of the body. It will be found that this connection enables us to express the definition of the absolute temperature by means of properties of the body that depend in a determinable way on the temperature τ.

The energy e of the body, and the pressure p supported by the body, are uniformly and continuously determined by the

thermodynamic state of the body. They can, therefore, be considered to be differentiable functions

$$e = e(v,\tau), \qquad p = p(v,\tau),$$

of the variables v,τ. Writing W,Q for the work and heat added to the body in any reversible change of its thermodynamic state beginning with the state of reference in which the energy e has the assigned value zero, the energy is a continuous function of W,Q,

$$e = W + Q;$$

and we have

$$de = dW + dQ.$$

This equation can be replaced by

$$de = -\,pdv + \vartheta ds,$$

$$(4) \qquad = \left(-p + \vartheta\,\frac{\partial s}{\partial v}\right) dv + \vartheta\,\frac{\partial s}{\partial \tau}\,d\tau\,;$$

which, as stated, connects the absolute temperature with the energy. Since the second member of this equation is an exact differential, the connection may be expressed in the form

$$\frac{\partial^2 e}{\partial v \partial \tau} = \frac{\partial^2 e}{\partial \tau \partial v},$$

i. e., in the form

$$(5) \qquad \frac{\partial p}{\partial \tau} = \frac{d\vartheta}{d\tau}\,\frac{\partial s}{\partial v}.$$

This equation expresses the definition of the absolute temperature by means of thermodynamic properties of the body. For equating the heat-differential to ϑds expresses the definition of ϑ, and the relation of ϑ to τ is here connected with the thermodynamic properties $\partial p/\partial \tau$ and $\partial s/\partial v$ of the body. The quantity $\partial s/\partial v$, however, is not susceptible of direct experimental determination. But the relation, obtained from (4),

$$(6) \qquad \frac{\partial e}{\partial v} = -p + \vartheta\,\frac{\partial s}{\partial v},$$

connects it with quantities whose values *can* be found by experimental means; wherefore we find, on eliminating $\partial s/\partial v$ between (5), (6),

(7)
$$\frac{d \log \vartheta}{d\tau} = \frac{\dfrac{\partial p}{\partial \tau}}{\dfrac{\partial e}{\partial v} + p}.$$

This is the required differential equation for $\dot{\vartheta}$. From it, by integration, the desired form of the function $\vartheta(\tau)$ can be found, when the forms of the functions p and $\partial e/\partial v$ shall have been established with sufficient accuracy by experimental means. To this end it is necessary merely to determine the pressure of the mass of gas at different volumes and temperatures, and the quantities of heat that it absorbs when from different initial states it expands into a vacuum.

From a theoretical point of view, it is not without interest to note that introduction of the ' thermal coefficients '

$$c_\tau = \vartheta \frac{\partial s}{\partial v}, \qquad c_v = \vartheta \frac{\partial s}{\partial \tau},$$

transforms (4) to

$$de = (-p + c_\tau)dv + c_v d\tau \,;$$

whence

$$\frac{\partial e}{\partial v} = -p + c_\tau \,;$$

wherefore (7) becomes

$$\frac{d \log \vartheta}{d\tau} = \frac{1}{c_\tau} \frac{\partial p}{\partial \tau}.$$

This is a very simple form of the differential equation for ϑ ; but, as has been stated, the thermal coefficient c_τ, which is the rate at which heat is absorbed by the body in reversible expansion at constant temperature, is not susceptible of direct experimental determination.

4. Properties of the thermometric gas

For the purpose of integrating the differential equation for the absolute temperature, let us consider the forms that experiment has yielded for the functions p and $\partial e/\partial v$ of the variables v, τ.

It is observed that the pressure of a given mass of any one of the more permanent gases varies approximately inversely as

the volume of the mass when the temperature is constant. We thus have the 'law of Boyle,'

(8) $$p\,v = f(\tau).$$

Further, the equation

$$\tau = \frac{273}{v_0}\,v,$$

expressing the 'law of Gay-Lussac' and the definition of the scale of temperatures τ, may be written

$$\frac{v}{\tau} = \frac{v_0}{\tau_0}$$

(9) $$= \phi(p).$$

Eliminating the common variable v between (8), (9),

$$\frac{f(\tau)}{p} = \tau \cdot \phi(p)\,;$$

or, separating the variables,

$$\frac{f(\tau)}{\tau} = p \cdot \phi(p) = r\,;$$

where the two expressions, being functions of the separate variables, must be equal to the same constant r. This converts both (8) and (9) to

$$p\,v = r\,\tau\,;$$

where the quantity $r = pv/\tau$ is constant for a given mass of a given gas.

Another way of combining (8), (9) is to note that, from these respective equations,

$$\frac{\partial \log v}{\partial p} = -\frac{1}{p}$$

$$\frac{\partial \log v}{\partial \tau} = +\frac{1}{\tau}\,;$$

whence

$$d \log v = -\,d \log p + d \log \tau\,;$$

whence

$$pv = r\tau,$$

as before.

It has been observed,* further, that when a mass of a gas of the type under consideration expands adiabatically into a vacuum the temperature of the mass remains almost unchanged.   Disregarding the small variation of temperature actually observed, we have

$$e(v_2,\tau) - e(v_1,\tau) = 0 ;$$

whence follows

(10)
$$\frac{\partial e}{\partial v} = 0.$$

This equation expresses what is sometimes known as the 'law of Joule.'

The thermodynamic behavior of no gas conforms exactly to the 'laws' of Boyle, Gay-Lussac, and Joule.   But, under low pressures and over a very wide range of temperatures, the more permanent gases do behave very nearly as these laws prescribe.

5. The form of the absolute temperature

We are now in position to effect an approximately correct integration of the differential equation for the absolute temperature,

$$\frac{d \log \vartheta}{d\tau} = \frac{\dfrac{\partial p}{\partial \tau}}{\dfrac{\partial e}{\partial v} + p}.$$

If it be assumed that the thermodynamic behavior of the selected thermometric gas sensibly conforms to the law of Joule,

$$\frac{\partial e}{\partial v} = 0,$$

we shall have

$$\frac{d \log \vartheta}{d\tau} = \frac{\partial \log p}{\partial \tau} .$$

If, further, the behavior of the gas is in conformity with the laws of Boyle and Gay-Lussac, we have

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* By Gay-Lussac, and again much later by Joule.

$$p = \frac{r\tau}{v}, \quad \frac{\partial p}{\partial \tau} = \frac{r}{v}, \quad \frac{\partial \log p}{\partial \tau} = \frac{1}{\tau};$$

wherefore the differential equation for ϑ becomes

$$\frac{d \log \vartheta}{d\tau} = \frac{1}{\tau};$$

integration of which yields

$$\log \vartheta = \log \tau + \log a$$

(11) $$\vartheta = a\tau.$$

The value of the constant of integration a shall now be determined by the condition that the difference between the absolute boiling and freezing temperatures of water under the pressure of one atmosphere shall be one hundred degrees. We thus have, by (11),

$$\vartheta(373) = a \cdot 373$$
$$\vartheta(273) = a \cdot 273 ;$$

whence, by subtraction,

$$100 = a \cdot 100$$
$$a = 1.$$

Equation (11) accordingly becomes

$$\vartheta = \tau.$$

It thus appears that the scale of absolute temperatures is identical with the temperature scale of a constant pressure gas-thermometer filled with a gas whose thermodynamic behavior conforms to the laws of Boyle, Gay-Lussac, and Joule.

Over an extensive range of temperatures, a very good approximation to the scale of thermal levels, or absolute temperatures, is given by gas-thermometers filled with one of the more permanent gases, as hydrogen, or nitrogen, or air. To obtain a closer approximation, it is necessary to determine more accurately, for some gas, the forms of the functions p and $\partial e/\partial v$. Such experimental determinations are difficult, and they have not yet led to formulations that exhibit a high degree of accuracy throughout an extensive range of states.

6. Isothermal variations of the energy

We shall now examine a means of experimental study of the isothermal variations of the energy of a gas, when these variations do not vanish as is required by the law of Joule.   It will prove convenient to adopt p, τ as the independent variables whose values determine the thermodynamic state of unit mass of the given gas.   In these variables, the equation for the differential of the energy of the mass,

$$de = - p\,dv + \vartheta\,ds,$$

is the equation

$$(12) \quad de = \left(- p\,\frac{\partial v}{\partial p} + \vartheta\,\frac{\partial s}{\partial p}\right)dp + \left(- p\,\frac{\partial v}{\partial \tau} + \vartheta\,\frac{\partial s}{\partial \tau}\right)d\tau.$$

The condition,

$$\frac{d\vartheta}{d\tau}\frac{\partial s}{\partial p} = - \frac{\partial v}{\partial \tau},$$

for the integrability of the second member of (12), converts the equation

$$\frac{\partial e}{\partial p} = - p\,\frac{\partial v}{\partial p} + \vartheta\,\frac{\partial s}{\partial p}$$

to

$$\frac{\partial e}{\partial p} = - p\,\frac{\partial v}{\partial p} - \vartheta\,\frac{\partial v}{\partial \tau} : \frac{d\vartheta}{d\tau} ;$$

whence the differential equation for ϑ is obtained in the form

$$(13) \qquad \frac{d \log \vartheta}{d\tau} = \frac{- \dfrac{\partial v}{\partial \tau}}{\dfrac{\partial e}{\partial p} + p\,\dfrac{\partial v}{\partial p}}.$$

According to the law of Joule, the pressure derivative $\partial e / \partial p$ is zero.*   The actual value of this derivative, for a given

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* From $\epsilon = e(v, \tau)$ and $v = v(p, \tau)$ we have

$$\frac{\partial e(p, \tau)}{\partial p} = \frac{\partial e(v, \tau)}{\partial v}\frac{\partial v}{\partial p} ;$$

whence it appears that the law of Joule requires that $\partial e / \partial p = 0$.

gas in an assigned state, can be determined by causing the gas to stream through a porous plug (of fibrous material) in a thermally well insulated tube, and noting the pressure and temperature of the steady stream on each side of the plug. Disregarding the negligibly small kinetic energy, these quantities will determine the change of the energy of unit mass of the gas in passing from the one state to the other. From this change of energy, and the known specific heat of the substance, can then be obtained the change of the specific energy of the gas when its pressure is varied at constant temperature.

In Fig. 12 let the lines a,a and b,b denote the boundaries of unit mass of the gas before and after the plug; the first state being determined by p,τ, and the second by $p + \delta p$,

FIG. 12.

$\tau + \delta\tau$. Since an expression for $\partial e/\partial p$ is sought, a concluding change of temperature at constant pressure shall be supposed to bring the mass after the plug to the state $p + \delta p$, τ.

In the total process, whereby the mass is brought from the state p,τ to the state $p + \delta p$, τ, the change of the *energy* of the mass is

$$(14) \qquad e(p + \delta p, \ \tau) - e(p,\tau) = \frac{\partial e}{\partial p}\, \delta p\,;$$

by Taylor's theorem, neglecting terms of the second order.

The *work* added to the mass is the work $p \cdot v(p,\tau)$ of the pump maintaining the pressure p, less the work $(p + \delta p) \cdot v(p + \delta p, \tau + \delta\tau)$ of the mass issuing against the reduced pressure $p + \delta p$, i. e., together

$$- \delta(pv)\,;$$

less the product of the final pressure into the increase of volume $\partial v/\partial\tau(-\delta\tau)$ in the concluding change of temperature,

$$(p + \delta p)\frac{\partial v}{\partial\tau}\, \delta\tau.$$

The total work added is, thus,

$$- \delta(pv) + (p + \delta p) \frac{\partial v}{\partial \tau} \delta \tau$$

$$= - p \left(\frac{\partial v}{\partial p} \delta p + \frac{\partial v}{\partial \tau} \delta \tau \right) - v \delta p + p \frac{\partial v}{\partial \tau} \delta \tau$$

(15) $$= - \left(v + p \frac{\partial v}{\partial p} \right) \delta p.$$

Here, again, terms of the second order are neglected.

The *heat* added to the mass is added in the concluding change of temperature from $\tau + \delta \tau$ to τ at constant $p + \delta p$,

(16) $$\int_{\tau + \delta \tau}^{\tau} c_p d\tau = - c_p \delta \tau.$$

Now, from (14), (15), (16), by the first law of thermo-dynamics,

$$\frac{\partial e}{\partial p} \delta p = - \left(v + p \frac{\partial v}{\partial p} \right) \delta p - c_p \delta \tau ;$$

whence

(17) $$\frac{\partial e}{\partial p} = - \left(v + p \frac{\partial v}{\partial p} \right) - c_p \lim \frac{\delta \tau}{\delta p};$$

where $\delta p, \delta \tau$ are the observed changes of the pressure and temperature of the gas on passing the plug.

For a gas whose thermodynamic behavior conforms to the laws of Boyle, Gay-Lussac, and Joule, we have

$$v = \frac{r\tau}{p}, \qquad \frac{\partial v}{\partial p} = - \frac{r\tau}{p^2}, \qquad \frac{\partial e}{\partial p} = 0 ;$$

which values convert (17) to

$$0 = - \left(\frac{r\tau}{p} - \frac{r\tau}{p} \right) - c_p \lim \frac{\delta \tau}{\delta p};$$

whence, since $c_p \neq 0$,

$$\lim \frac{\delta \tau}{\delta p} = 0.$$

The temperature of such a gas would not alter on passing the porous plug.

If the expression given by (17) for the pressure derivative of the specific energy of the gas be introduced into the differential equation (13) for the absolute temperature,

$$\frac{d \log \vartheta}{d\tau} = \frac{-\dfrac{\partial v}{\partial \tau}}{\dfrac{\partial e}{\partial p} + p \dfrac{\partial v'}{\partial p}}$$

we obtain

(18)
$$\frac{d \log \vartheta}{d\tau} = \frac{\dfrac{\partial v}{\partial \tau}}{v + c_p \lim \dfrac{\delta\tau}{\delta p}}$$

$$= \frac{\dfrac{\partial \log v}{\partial \tau}}{1 + \dfrac{c_p}{v} \lim \dfrac{\delta\tau}{\delta p}}.$$

The accuracy of the form of the function $\vartheta(\tau)$ obtained by integration of this equation will depend on the accuracy with which the forms of the functions

$$v(p,\tau), \quad c_p(p,\tau), \quad \lim \frac{\delta\tau}{\delta p},$$

will have been obtained by experiment.*

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* In the experiment with the porous plug, the change of state of the gas satisfies a very simple general equation. When the stream has reached a 'steady state,' the work added to unit mass of the gas in the operation of passing the plug is the work

$$p \cdot v(p,\tau)$$

of the pump maintaining the pressure p, less the work

$$(p + \delta p) \cdot v(p + \delta p, \tau + \delta\tau)$$

done by the mass in issuing against the reduced pressure $p + \delta p$; i. e., together,

$$- \delta(pv).$$

In so far as the operation really is adiabatic, the change of the energy of unit mass of the gas on passing from the steady state 1 before the plug to the steady state 2 after the plug is, then,

$$e_2 - e_1 = - p_2 v_2 + p_1 v_1 ;$$

which relation may be written

7. Summary of Chapter IV.

It is sought to connect the absolute temperature ϑ with the temperatures τ of the scale of a constant pressure gas-thermometer. To accomplish this, the definition of ϑ must be expressed by means of the thermodynamic properties of some aeriform body.

Within the region of realizable aeriform states of the selected thermometric body, the absolute temperature and the entropy of the body are differentiable functions $\vartheta(\tau)$, $s(v,\tau)$. Consequently, the definition

$$dQ = \vartheta ds$$

of the absolute temperature becomes

$$ds = \frac{c_\tau dv + c_v d\tau}{\vartheta},$$

and asserts that ϑ is an integrating divisor of the heat-differential of the body with regard to reversible changes of state. This assertion uniquely defines ϑ, since ϑ is a function of τ alone.

The two laws of thermodynamics, as expressed by

$$de = - pdv + \vartheta ds,$$

connect the absolute temperature and the energy of the body. This connection, in the form

$$\frac{\partial^2 e}{\partial v \partial \tau} = \frac{\partial^2 e}{\partial \tau \partial v},$$

i. e., in the form

$$\frac{\partial p}{\partial \tau} = \frac{d\vartheta}{d\tau} \frac{\partial s}{\partial v},$$

expresses the definition of ϑ by means of thermodynamic properties of the thermometric body. By means of the relation

$$\frac{\partial e}{\partial v} = - p + \vartheta \frac{\partial s}{\partial v},$$

the connection in question is made to express the definition of

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$$e_2 + p_2 v_2 = e_1 + p_1 v_1.$$

If we write g for the quantity $e + pv$, this equation of the process is simply

$$g_2 = g_1.$$

It has been proposed by Kamerlingh Onnes to term the quantity g, Gibbs's specific *heat function for constant pressure*, the specific *enthalpy* of the gas.

ϑ by means of quantities whose values can be determined by experimental means,

$$\frac{d \log \vartheta}{d\tau} = \frac{\partial p}{\partial \tau} : \left(\frac{\partial e}{\partial v} + p \right).$$

When this equation is integrated under the assumption that the thermodynamic behavior of the selected thermometric gas sensibly conforms to the laws of Boyle, Gay-Lussac, and Joule, it is found that the scale of absolute temperatures is identical with the temperature scale of a constant pressure gas-thermometer filled with the gas.

To obtain a more accurate result, more accurate formulation of the functions p, $\partial e/\partial v$ is necessary. The quantity $\partial e/\partial v$ is not susceptible of accurate experimental determination. But the values of the equivalent $\partial e(p,\tau)/\partial p$ can be deduced from observations of the changes of pressure and temperature exhibited by the gas when streaming adiabatically through a porous plug; whereupon the relation of the absolute temperature to the temperature of the gas-thermometer filled with the gas is to be obtained by integrating the equation in p,τ,

$$\frac{d \log \vartheta}{d\tau} = - \frac{\partial v}{\partial \tau} : \left(\frac{\partial e}{\partial p} + p \frac{\partial v}{\partial p} \right).$$

CHAPTER V. Dissipation

The *reversible* processes considered in the preceding chapters consist of successions of quiescent states. They are not actual physical processes. Every actual thermodynamic change of state is a spontaneously occurring change of the thermodynamic state of the body composed of all the bodies participating in the process. It is an *irreversible*, adiabatic, isodynamic * operation. And it can always be utilized for the production of work. Let us support this statement by the consideration of some typical cases.

A heavy ball falls into a thermally isolated receptacle, and the common temperature of the ball and receptacle rises in consequence of the impact. If a cord passing over a pulley is attached to the ball, the process may be made to yield work, as in raising another body. In this way the spontaneous process may be retarded, until it becomes reversible when the weight of the body raised is but infinitesimally less than that of the ball. In this operation the energy of the ball is decreased by the amount of the work developed ; and the final state reached in the wholly irreversible operation can be reversibly attained by reversible addition of a quantity of heat equal to the work developed.† In consequence, over the *reversible* path between the end states,

$$S \frac{dQ}{\vartheta} > o \, ;$$

in the spontaneous process the ball and receptacle pass to a state whose entropy is greater than that of the initial state.

Another spontaneous change of state is the adiabatic expansion of a mass of gas into an exhausted receiver. In the final state, the temperature of the mass may prove to be either less than, or equal to, or greater than the initial temperature. When the adiabatic change of volume is conducted reversibly, through expansion behind a piston against a pressure maintained

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* Occurring at constant energy.

† Such addition of heat may be effected through reversible compression of a contiguous mass of fluid, — say a mass of some gas or of coexistent liquid and vapor.

infinitesimally less than the pressure exerted by the mass of gas, work is developed at the expense of the energy of the mass of gas, and the final temperature is lower than before. Reversibly to attain the former final state, a quantity of heat equal to the work developed must be reversibly added. Over the reversible path between the end states,

$$S \frac{dQ}{\vartheta} > 0;$$

in the spontaneous process the mass of gas passes to a state whose entropy exceeds that of the initial state.

The outcome is the same when the spontaneous change of state of the mass of gas is an adiabatic compression. Let the mass be contained in a vertical cylinder under a frictionless piston whose weight w per unit area a of its under surface is greater than the initial value p_1 of the pressure p of the gas,

$$w/a > p_1.$$

On releasing the piston, irreversible adiabatic compression of the gas ensues ; and, when the system of bodies comes to rest, the pressure w/a exerted by the piston is counterbalanced by the pressure p_2 of the gas. Let it be supposed that no sensible transfer of heat from the gas to the cylinder and piston occurs.
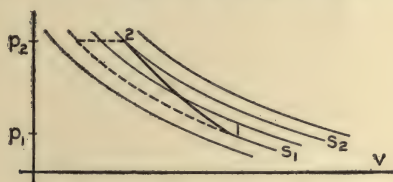
FIG. 13.

Now, on a *reversible* path between the end states of the system of bodies, consider a reversible adiabatic compression of the gas to occur as the fall of the piston is retarded by a force but infinitesimally less than $w/a - p$. The entropy s_1 of the gas remains unchanged. At the close of the compression, the pressure w/a exerted by the piston is counterbalanced by the pressure p_2 of the gas, and work has been developed at the expense of the energy of the gas. Reversibly to restore the system to its former final state, a quantity of heat equal to the work developed must be reversibly added to the gas ; on the reversi-

ble path between the end states, the gas passes to a state of increased entropy. In the irreversible process, therefore, the entropy of the final state of the gas necessarily exceeds that of the initial state.

Another spontaneous change of state is the equalization of the initially different temperatures of two metal blocks. This adiabatic change of state of the blocks can be conducted reversibly through intervention of a succession of cyclical operations (see p. 32), in which heat is absorbed from the hot block and is transmitted to the cold one.* When the hot block reaches the final temperature attained in the irreversible process, some of the heat developed by it has been converted into work, and less than before has been transmittted to the cold block. In order to equalize the temperatures, the succession of cycles must be continued, with further development of work and the attainment of a lower final temperature of the blocks than before. Reversibly to attain the former final state, a quantity of heat equal to the work developed must be reversibly added to the blocks. Over the reversible path between the end states,

$$S \frac{dQ}{\vartheta} > 0 \, ;$$

in the spontaneous process the blocks pass to a state whose entropy exceeds that of their initial state.

Yet another spontaneous change of state is the dilution of an aqueous solution of cane sugar by an added mass of water. When this irreversible adiabatic process is conducted reversibly (see p. 55), by means of a semipermeable piston, work is gained and the energy of the liquid mass is decreased by the amount of the work developed. Reversibly to restore the mass to the final state attained in the irreversible process, a quantity of heat equal to the work developed must be reversibly added. Over the reversible path between the end states,

$$S \frac{dQ}{\vartheta} > 0 \, ;$$

in the spontaneous process the liquid mass passes to a state whose entropy exceeds that of the initial state.

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* Refer to page 34, where it was remarked that " The final temperature of the blocks is not the temperature that would have been attained had the process occurred in a wholly spontaneous way — without development of work. The bearing of this important observation will be made the subject of Chapter V."

From illustrations such as these is drawn the general con-
clusion that any spontaneously occurring change of the thermo-
dynamic state of a body can be utilized for the production of
work. The assemblage of all the bodies participating in the
operation may be regarded as a dynamically and thermally
isolated body. If the change of state of this isolated body is
conducted in a reversible (controlled) manner, the maximum
work that the process can yield is gained; if the change occurs
in a wholly irreversible (uncontrolled, or spontaneous) manner,
the maximum work-developing ability that the body can lose
is lost, being 'dissipated' in transfers of heat. In the rever-
sible process, the energy of the whole body is decreased by the
amount of the work that is developed; wherefore the final
state attained in the irreversible process can be *reversibly*
reached on addition, to the body, of the positive quantity of
heat equivalent to this work. In consequence, the limit,

$$\mathrm{S}\frac{dQ}{\vartheta},$$

taken over any reversible path between the two end states,
necessarily has a positive value.

In other words, whenever an isolated body suffers an irre-
versible (uncontrolled, or spontaneous) change of state, the
body passes to a state in which its entropy is *greater* than its
entropy in the initial state. This statement might very well
be termed the Third Law of Thermodynamics. Were it so
termed, the general principles of thermodynamics would be
expressed by three 'laws': the energy law, the entropy law,
and the dissipation law. Although this is the most instructive
view of the matter, the term 'third law of thermodynamics' is
not in use.

CHAPTER VI. Summary of Book I.

Thermometry

Any measurable physical property of a body, that is a continuous, uniform, and increasing (or decreasing) function of the degree of hotness of the body, is a *thermometric property* of the body. Any uniform, analytic, and increasing (or decreasing) function of a chosen thermometric property of a chosen substance defines a scale of the *temperatures* of the body. The scale of temperatures,

$$\tau = \frac{273}{v_0} v,$$

of a constant pressure gas-thermometer is defined in this way.

Physical Processes

An ensemble of changes of the physical properties of an assemblage of bodies is a *physical process*. Physical processes may be classified in accordance with the degree in which the physical character of the participating bodies is modified. Of all physical processes the *mechanical processes* are the least deep seated. In any purely mechanical process the sum of the potential and kinetic energies of the participating bodies remains constant.

Changes of State

A *body* is a material object or assemblage of objects, from which no portion is removed and to which no extraneous matter is added. When the physical character of a body undergoes no alteration, the body is in a (quiescent) physical *state*. When the body passes from one state to another it undergoes a definite *change of state*. The *path* of an actual change of state is the actual succession of 'non-quiescent states.' A continuous succession of quiescent states — of 'states' — is a *reversible path*. With reference to any given change of the physical state of a body, the *supplementary change of state* is the associated change of state of the body composed of all the other bodies in any way participating in the process.

Mechanical Aspects of Changes of State

Many supplemented changes of the physical states of bodies can be brought 'directly' (without intervention of an intermediate change of state), or 'indirectly' (through intervention of friction), or both directly and indirectly, into exclusive connection with mechanical operations. Every such change of state is directly supplemented, wholly or in part or not at all, by a mechanical operation ; and, in so far as it is not so supplemented, it either is or can be supplemented by a mechanical operation acting through intervention of friction, or it can be replaced by a mechanical operation acting through intervention of friction.

When two bodies undergo such mutually supplementary changes of state, the quantity of mechanical energy developed by either one of the bodies is the *quantity of mechanical energy added* to the other. And the mechanical energy developed in the mechanical operation that can for the rest supplement one of the changes of state and replace the other, on the actual paths of these changes of state, is the *quantity of heat added* to the body undergoing the supplemented change of state, and is the negative of the quantity of heat added to the body undergoing the replaced change of state.

Thermodynamic Changes of State

We are concerned, then, with supplemented changes of state, not purely mechanical, that can be brought directly or indirectly or both directly and indirectly into connection with mechanical operations. The states of a body, attainable through such changes of state, constitute the continuous assemblage of the *thermodynamic states* of the body. All such changes of state, and also all possible changes of the state of an *isolated* body from one thermodynamic state to another, are *thermodynamic changes of state*. The study of thermodynamic changes of state is *thermodynamics*.

The First Law of Thermodynamics

It is sought to establish a quantitative formulation of thermodynamic changes of state, through examination of the relations that these processes bear to mechanical changes of state. To this end, it is sought to define the 'energy of a body' in such a way that the total energy of the bodies participating in any

thermodynamic process will remain constant.   If such a quantity exists, it must satisfy the definition : The *energy* of a body in any thermodynamic state x is a quantity $E_x + E_o$, whose change U_{ab} when the body undergoes a change of thermodynamic state from the state a to the state b is equal to the algebraic sum of the quantities of mechanical energy M_{ab} and heat Q_{ab} added to the body in the course of the change of state,

$$(E_x + E_o)\Big|_a^b = U_{ab}$$

$$= M_{ab} + Q_{ab}.$$

To establish whether U_{ab} is equal to the change of a quantity $E_x + E_o$ whose value, save for an arbitrary additive constant, is uniquely determined by the thermodynamic state x of the body, it is necessary and sufficient to establish that U_{ab} is independent of the path of the change of state ab.   That this condition is satisfied is indicated by the results of extended experimental study of processes in which mechanical operations supplement changes of the temperatures and changes of the states of aggregation of bodies, and of processes in which various changes of thermodynamic state supplement changes of the temperatures of other bodies and often mechanical actions as well.   It is held, therefore, that

$$E_b - E_a = M_{ab} + Q_{ab} ;$$

which equation expresses the *first law of thermodynamics*.   This great generalization is abundantly justified by the extended and exact agreement of its consequences with experience. The agreement is certainly within the limits of experimental error.

The heat-unit determined by the quantity of mechanical energy requisite to raise unit mass of water through the temperature interval $\tau - \tau_r = 1$ is the *calory*.   When expressed in mechanical units, the calory is often termed the *mechanical equivalent of heat*.   It is, practically, the 'specific heat' of water at τ_r.

Formulation of Heat Transfers

In order to express the first law of thermodynamics,

$$E_b - E_a = M_{ab} + Q_{ab},$$

by means of quantities determined by the thermodynamic state of the body undergoing the change of state *ab*, it is necessary to express the terms M_{ab} and Q_{ab} by means of such quantities. With regard to a *reversible* path, the quantity M_{ab} is the *work* W_{ab} of forces supported by the body. The work of such a force is the product of the force into the effected displacement; and the force and the displacement are quantities that are determined by the state of the body. The work W_{ab} depends in general on the path; therefore the concurrent transfer of heat Q_{ab} depends on the path. It is required to show whether this transfer of heat can be expressed by means of quantities determined by the thermodynamic state of the body.

The operation of a Carnot cycle of thermodynamic changes of the state of a body is analogous to the operation of a freight elevator transporting an increment of load between different heights. In the case of the elevator, when the heights and the transferred quantities of potential energy and of work are given, the transfers of potential energy can be analytically expressed, through the formulation

$$dQ = \vartheta dS,$$

by means of quantities that are uniquely determined by the state of the elevator, and whose values can be found from the given data. In the analogous thermodynamic case, when the temperatures and the transferred quantities of heat and of work are given, is the relation

$$dQ = \vartheta dS$$

satisfied by quantities ϑ, S that are uniquely determined by the state of the working body, and whose values can be found from the given data?

The Thermal Level of a Body

Pursuing the guiding analogy, the increase $\vartheta_n - \vartheta$ of *thermal level* corresponding to any increase $\tau_n - \tau$ of temperature is defined by the number of Carnot cycles in any 'series' of such cycles between the two temperatures, — and the level unit is arbitrary. From the *principle* that an isothermal development of heat cannot supplement an absorption of work is deduced the *theorem of Carnot*, that, with reference to any Carnot cycle absorbing Q at τ, absorbing W, and operating between τ, τ_n, the ratio Q/W is determined by τ, τ_n. From the theorem of Carnot it follows that $\vartheta_n - \vartheta$ is determined by τ, τ_n.

If the posited relation

$$dQ = \vartheta dS$$

is satisfied by quantities ϑ, S determined by the state of the body, the relation

(1) $$Q_{\alpha\beta} = \vartheta(S_\beta - S_\alpha)$$

must be satisfied. In particular, $Q_{\alpha\beta}$ must be independent of the isothermal path $\alpha\beta$. It follows from Carnot's theorem that this requirement is fulfilled. Further, on a reversible adiabatic path, S must satisfy $dS = 0$; wherefore the relation

(2) $$W[Q_{\alpha\beta},1°] = S_\beta - S_\alpha$$

must be satisfied. Since both (1), (2) must be satisfied, it follows that ϑ must satisfy

$$\vartheta = Q_{\alpha\beta}/W[Q_{\alpha\beta},1°].$$

By Carnot's theorem, the thermal level ϑ defined by this equation is determined by τ alone.

The Thermal Load of a Body

It remains to establish whether the relation

$$dQ = \vartheta dS$$

is satisfied by the differential of a quantity S that is uniquely determined by the thermodynamic state of the body and can be found from the given data. In any Carnot cycle in which the working body absorbs Q at τ and absorbs $-Q_n$ at τ_n, the thermal levels ϑ, ϑ_n are

$$\vartheta = Q/W, \qquad \vartheta_n = Q_n/W;$$

whence

$$\frac{Q}{\vartheta} + \frac{Q_n}{\vartheta_n} = 0.$$

If *any* reversible closed path of change of the thermodynamic state of the body can be approximated by a succession of isothermal and adiabatic paths belonging to a succession of Carnot cycles; and if the quantity of heat absorbed on the closed path is the limit of the sum of the quantities of heat absorbed on the broken path; which assumptions appear to be fulfilled; we shall have

$$S \frac{dQ}{\vartheta} = 0,$$

the summation being taken over the closed path. It follows that the expression dQ/ϑ is equal to the differential of a quantity S determined by the thermodynamic state of the body. This conclusion is the *second law of thermodynamics*.

It thus appears that the thermodynamic state of a body uniquely determines quantities ϑ,S that can be found from the given data and are such that

$$dQ = \vartheta dS.$$

Accordingly, in the formulation

$$Q_{ab} = \int_a^b \vartheta dS,$$

any reversible transfer Q_{ab} of heat to or from the body, on any assigned path $\phi(\vartheta,S) = 0$, is analytically expressed by means of quantities determined by the thermodynamic state of the body. In consequence, in the equation

$$E_b - E_a = W_{ab} + \int_a^b \vartheta dS,$$

the first law of thermodynamics is expressed by means of such quantities. The 'thermal level' ϑ and the 'thermal load' S are the *absolute temperature* and the *entropy* of the body.

Determination of Absolute Temperatures

To connect the absolute temperature ϑ with the temperatures τ of the scale of a constant pressure gas-thermometer, the definition of ϑ must be expressed by means of thermodynamic properties of some aeriform body.

Within the region of realizable aeriform states of the selected thermometric body, the absolute temperature and the entropy of the body are differentiable functions $\vartheta(\tau)$, $s(v,\tau)$. Consequently, the definition

$$dQ = \vartheta ds$$

of the absolute temperature becomes

$$ds = \frac{c_\tau dv + c_p d\tau}{\vartheta},$$

and asserts that ϑ is an integrating divisor of the heat-differential of the body with regard to reversible changes of state. This assertion uniquely defines ϑ, since ϑ is a function of τ alone.

The two laws of thermodynamics, as expressed by

$$de = - \, pdv + \vartheta ds,$$

connect the absolute temperature and the energy $e(v,\tau)$ of the body. This connection, in the form

$$\frac{\partial^2 e}{\partial v \partial \tau} = \frac{\partial^2 e}{\partial \tau \partial v},$$

i. e., in the form

$$\frac{\partial p}{\partial \tau} = \frac{d\vartheta}{d\tau} \frac{\partial s}{\partial v},$$

expresses the definition of ϑ by means of thermodynamic properties $\partial p / \partial \tau$ and $\partial s / \partial v$ of the body. By means of the relation

$$\frac{\partial e}{\partial v} = - \, p + \vartheta \frac{\partial s}{\partial v},$$

the connection in question is made to express the definition of ϑ by means of quantities whose values can be determined by experimental means,

$$\frac{d \log \vartheta}{d\tau} = \frac{\partial p}{\partial \tau} \left/ \left(\frac{\partial e}{\partial v} + p \right) \right. .$$

The accuracy of the form of $\vartheta(\tau)$ to be obtained by integration of this differential equation for the absolute temperature depends, of course, on the accuracy with which the forms of the functions p and $\partial e / \partial v$ shall have been determined by experiment. It appears that, if a constant pressure gas-thermometer could be filled with with a gas whose thermodynamic behavior should conform to the 'laws' of Boyle, Gay-Lussac, and Joule, the temperature scale of this thermometer would be identical with the scale of absolute temperatures, — unit difference of temperature being determined in the same way for both scales.

Dissipation

Reversible processes consist of successions of quiescent states. They are not actual processes. Every *actual* thermodynamic

change of state is a spontaneously occurring change of the thermo-dynamic state of the body composed of all the bodies partici-pating in the process ; it is an *irreversible* change of the state of a dynamically and thermally *isolated* body.

Every change of the thermodynamic state of an isolated body can be utilized for the production of work. If the actual change of state *ab* be conducted on a *reversible* path, work is gained at the expense of the energy of the body ; and this loss of energy must be made up by addition, to the body, of the positive quantity of heat equivalent to this work. It follows that, when an isolated body passes irreversibly from the ther-modynamic state *a* to the thermodynamic state *b*, the state *b* is necessarily such that

$$S_b - S_a > 0.$$

BOOK II. THE THERMODYNAMICS OF BODIES SUBJECT TO NO FORCE OTHER THAN A UNIFORM AND NORMALLY DIRECTED PRESSURE

PART I. GENERAL APPLICATION OF THE PRINCIPLES

CHAPTER I. THE CRITERION OF EQUILIBRIUM AND STABILITY

1. The stability of thermodynamic states

In the foregoing discussion, the general principles of the thermodynamics of bodies subject to the action of any mechanical forces have been given expression in three laws : the energy law, the entropy law, and the dissipation law. We shall now consider the bearing of these laws upon the thermodynamic behavior of bodies that may be assumed to be subject to no force other than a uniform and normally directed pressure. In particular, the influence of gravity upon this behavior shall be assumed to be negligible.

It will be noted, at the outset, that an isolated body when in certain thermodynamic states is capable of spontaneous changes of state, while in other states it is incapable of such changes. Consider any body in any definite thermodynamic state. If the body be encased in a rigid, thermally non-conducting shell, it becomes a dynamically and thermally *isolated* body, and its state remains unaltered. In this state, the body may be incapable of an irreversible change of state ; or it may be capable of such a change. If it be capable of such a change, it may be that the change will originate spontaneously, or it may be that occurrence of the process is prevented by some existing passive resistance to change. In the *absence* of a passive resistance, different parts of the body may exert different pressures, which will immediately become equalized ; or they may exhibit different temperatures, which will at once tend to attain a common value ; or the body may be a mass of liquid just beginning evaporation into an exhausted space ; or it may just be entering upon a slow or a turbulent chemical reaction. In the *presence* of a passive resistance, it may be that parts of the body

exerting different pressures are separated by rigid walls ; or that parts of the body having different temperatures are separated by non-conducting walls ; or that separated parts of the body are capable of forming homogeneous mixtures, or of reacting chemically ; or that a liquid and its vapor coexist at a temperature below the freezing temperature of the liquid (are ' supercooled ') ; or that a mass of detonating gas or of dynamite remains quiescent in the absence of any circumstance capable of producing an explosion. In every such case, the possible irreversible change of the thermodynamic state of the body can be initiated by some means ; and when this is done the process will proceed spontaneously until a state is attained where further spontaneous change is impossible.

When a body, under the conditions imposed upon it, is incapable of a spontaneous change of its thermodynamic state, the state is said to be *stable ;* in the contrary case the state is said to be *instable.* An isolated body in an instable state can be made to furnish a supply of work ; in a stable state it cannot be made to furnish a supply of work — it is in a state of ' dissipated energy.'

2. The criterion of stability

In any stable state, a body has a uniform pressure and a uniform temperature. If the body be enclosed in a flexible, freely extensible envelope surrounded by an elastic medium having the same uniform pressure and temperature, the state of the body will remain stable. Let it be supposed, now, that any chosen body enclosed in such an envelope surrounded by such a medium is initially in any state that *is not* a stable state under the pressure p of the medium at the temperature ϑ of the medium. A spontaneously occurring change of the thermodynamic state of the enclosed body will ensue, either spontaneously initiated or suitably induced ; and the body will thereby attain a state that is a stable state under the pressure p at the temperature ϑ. Let us examine what information concerning this process is afforded by the principles of thermodynamics.

It shall be supposed that the envelope is impermeable by any of the substances with which it is in contact, that it yields with extreme slowness under differences of pressure, and that it permits only extremely slow equalization of differences of temperature. It shall also be supposed that its compressibility and heat capacity are negligible ; wherefore a change of the energy of

the envelope does not come into consideration. The medium surrounding the envelope shall be understood to be of such extent that its pressure and temperature maintain the sensibly constant values p, ϑ.

Let the initial volume, entropy, and energy of the enclosed body be V_1, S_1, E_1, and the final values of these quantities be V, S, E. And let the volume, entropy, and energy of the medium change from $\mathbf{V}_1, \mathbf{S}_1, \mathbf{E}_1$, to $\mathbf{V}, \mathbf{S}, \mathbf{E}$. The change occurring in the state of the medium is reversible, because of the manner in which the envelope acts. Accordingly,

$$d\mathbf{E} = -pd\mathbf{V} + \vartheta d\mathbf{S};$$

whence, by integration,

$$\mathbf{E} - \mathbf{E}_1 = -p(\mathbf{V} - \mathbf{V}_1) + \vartheta(\mathbf{S} - \mathbf{S}_1).$$

Rearranging the terms of this equation, ·

$$\mathbf{E} + p\mathbf{V} - \vartheta\mathbf{S} = \mathbf{E}_1 + p\mathbf{V}_1 - \vartheta\mathbf{S}_1.$$

Now, the total energy and the total volume of the participating bodies do not alter in the process that occurs; their total entropy, however, increases by an amount Σ. We thus have,

$$
\begin{aligned}
-\mathbf{E} - E &= -\mathbf{E}_1 - E_1 \\
-p\mathbf{V} - pV &= -p\mathbf{V}_1 - pV_1 \\
\vartheta\mathbf{S} + \vartheta S &= \vartheta\mathbf{S}_1 + \vartheta S_1 + \vartheta\Sigma .
\end{aligned}
$$

Adding the *four* equations, we find

$$E_1 + pV_1 - \vartheta S_1 = E + pV - \vartheta S + \vartheta\Sigma;$$

or

$$E_1 - E = -p(V_1 - V) + \vartheta(S_1 - S) + \vartheta\Sigma.$$

In addition to the essentially positive quantity $\vartheta\Sigma$, this formulation involves only quantities relating to the end states of the body within the envelope. It may be written

$$\delta E = -p\delta V + \vartheta\delta S + \vartheta\Sigma,$$

where the operator δ relates to a variation of the state of the enclosed body *from* the stable state at p, ϑ *to* any state that is not a stable state at p, ϑ. The variation need be *physically realizable* only in the opposite sense: in that of the change from the

'varied state' (V_1, S_1, E_1) to the stable state (V, S, E). The term $\vartheta\Sigma$ being positive, we have

(1) $$\delta E + p\delta V - \vartheta\delta S > 0.$$

It thus appears that, when the body within the envelope has the uniform pressure p and the uniform temperature ϑ, the thermodynamic state of the body is a stable state if all possible variations of the energy, volume, and entropy of the body satisfy the inequality (1).

The above reasoning does not take into consideration the case in which the body is capable of a continuous succession of stable states at p,ϑ. Such a succession is traversed in the reversible evaporation of a given mass of a one-component fluid (e. g., of water) at an assigned temperature. In this case the body will pass spontaneously from no state of the succession to another state. If the change through the intervening succession of stable states be reversibly effected, we shall have

$$S + S = S_1 + S_1,$$

and so, in the calculation executed above,

$$E_1 + pV_1 - \vartheta S_1 = E + pV - \vartheta S,$$

or

$$\delta E + p\delta V - \vartheta\delta S = 0.$$

Combining both cases in one formulation, it appears that, when a body having the uniform pressure p and the uniform temperature ϑ is enclosed in the envelope here considered, the thermodynamic state of the body is stable if all possible variations of the energy, volume, and entropy of the body satisfy the **criterion of stability,**

$$\delta E + p\delta V - \vartheta\delta S \geq 0.$$

3. Stability under imposed conditions

With reference to any variation from a state that is stable at p,ϑ to a state that is not stable at p,ϑ, we have

$$\delta E + p\delta V - \vartheta\delta S > 0.$$

If the stable state and the varied state have:

The same E,V, the criterion becomes $\qquad\qquad \delta S < 0$

"   "   V,S,   "   "   " $\qquad\qquad \delta E > 0$

The same V, ϑ, the criterion becomes $\qquad \delta(E - \vartheta S) > 0$

" " p, S, " " " $\qquad \delta(E + pV) > 0$

" " p, ϑ, " " " $\qquad \delta(E + pV - \vartheta S) > 0$.

It thus appears that, under assigned conditions of unvaried energy and volume, stable equilibrium ensues when the entropy of the body is a maximum; it ensues at assigned volume and entropy when the energy is a minimum; at assigned volume and temperature when the quantity $E - \vartheta S$ is a minimum; at assigned pressure and entropy when the quantity $E + pV$ is a minimum; and at assigned pressure and temperature when the quantity $E + pV - \vartheta S$ is a minimum. Yet, of course, none of these particular conditions need be imposed. The varied state may in general be any thermodynamic state whatsoever.

4. Summary of Chapter I.

The thermodynamic state of a body is 'stable' when the body, under the conditions imposed upon it, is incapable of a spontaneous change of state. When the body is in a stable state, its pressure and temperature are uniform throughout.

Application of the energy law, the entropy law, and the dissipation law to an irreversible process conducting a body to a stable state at an assigned temperature under an assigned pressure yields the equations

$$E + pV - \vartheta S = E_1 + pV_1 - \vartheta S_1$$
$$E + \quad E = E_1 + E_1$$
$$V + \quad V = V_1 + V_1$$
$$S + \quad S = S_1 + S_1 \quad + \Sigma.$$

From these equations it follows that the thermodynamic state of a body supporting the uniform pressure p and having the uniform temperature ϑ of the contiguous bodies is stable if in every possible variation of the state the concurrent variations of the energy, the volume, and the entropy of the body satisfy the 'criterion of stability,'

$$\delta E + p \delta V - \vartheta \delta S \geq 0.$$

In this criterion, the quantities p, ϑ are the *constant* pressure and temperature of the given state. When the varied state is not stable under the imposed conditions, the sign of inequality obtains; when the varied state is stable under these conditions, the sign of equality obtains.

CHAPTER II. ANALYTICAL FORMULATION OF THE ENERGY AND ENTROPY LAWS

1. The problem

It will be of advantage, at this point, to recapitulate the results of the preceding discussion of the first and second laws of thermodynamics. The energy of a body subject to changes of thermodynamic state depends on the work W and heat Q absorbed by the body on any reversible path from a state of reference; and the application of the energy law to the body is expressed by the equation

$$E = W + Q.$$

Hence follows

$$dE = dW + dQ.$$

We are at present concerned with the application of this differential equation to the thermodynamic behavior of a body subject to no force other than a uniform and normally directed pressure p. For this case it is desired to express the equation by means of quantities that are determined by the state of the body. The quantities W, Q are not so determined, the independent differentials dW, dQ are not the differentials of quantities determined by the state. Yet these differentials can be expressed by means of such quantities. In the formulations

$$dW = -pdV, \quad dQ = \vartheta dS,$$

they are expressed by inexact differential expressions in quantities p, V and ϑ, S that depend solely on the thermodynamic state of the body. For, by the first law of thermodynamics, the energy E of the body is uniquely determined by this state; by the second law, the absolute temperature ϑ and the entropy S are determined by the state; and, according to physical experience, the pressure p and the volume V of the body are determined in the same way. Therefore, in the equation

$$(1) \qquad dE = -pdV + \vartheta dS,$$

the energy and entropy laws are analytically expressed by means of quantities that are determined by the state of the body to whose thermodynamic behavior the equation is applied.

Now, although in equation (1) the two laws of thermody-
namics are expressed by an analytical relation between quantities

$$E, p, V, \vartheta, S,$$

that are determined by the state, yet these laws are not ex-
pressed by a relation between analytic functions of independent
measurable physical quantities (variables) that determine the
state. If the *physical quantities* in question could be replaced
by such *functions*, the equation

$$dE = -\,pdV + \vartheta dS$$

would afford an analytical theory of the thermodynamic behavior
of the body. For it would express this behavior by means of
relations between the pressure and temperature of the body
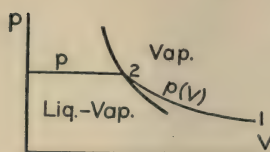and the volumes, masses, and compositions of its several homo-
geneous parts.

2. The general state of a body

We are thus led to enquire whether it is practicable to ex-
press the quantities

$$E, p, V, \vartheta, S,$$

by analytic functions of variables that determine the general
state of the given body.

In different regions of the thermodynamic state of a given
body, the body appears in different 'states of aggregation.'
Thus in one such region the body may consist of a homogene-
ous mass of vapor; in a contiguous region it may consist of
coexisting masses of liquid and vapor.
Within any such region of states, work
and heat are absorbed by the body at
continuous rates on any reversible path;
but these rates are observed to be dis-
continuous when the body passes from
one region to another. For example,
in a reversible isothermal compression of a vapor from a state
1, the work absorbed by the compressed body is

$$-\int_1^V p(V)dV,$$

where the continuous function $p(V)$ is the pressure supported

by the body at states on the isotherm. In a like compression of the coexisting liquid and vapor, from a state 2 on the boundary of the region of coexistent liquid and vapor, the work absorbed is

$$-\int_2^V p\,d\mathrm{V},$$

where p is the constant vapor pressure of the body. At the point 2, the rate at which work is absorbed, per unit isothermal change of volume, changes *discontinuously* from the variable value $p(\mathrm{V})$ to the constant value p.

Again, it does not appear that the states of *different* regions of the state of a given body can be specified by values of the *same* physical variables. For example, any homogeneous state of a given mass of water is determined by any two of the three variables, the pressure p, the volume V, and the temperature τ of the body; but the variables p, τ cannot be chosen to determine a state of coexisting liquid and vapor, since when both p and τ are constant the masses of liquid and vapor can coexist in any ratio; and no combination of the variables determines a state of coexisting ice, liquid, and vapor, since this state can be varied by heating without altering the value of any of the variables.

Since, then, the state of a body may change *discontinuously* when the body passes from one continuous region of thermodynamic states to another; and since the general state of the body cannot be specified by a single set of independent physical variables; it seems to be impracticable to attempt to express the quantities

$$\mathrm{E}, \ p, \ \mathrm{V}, \ \vartheta, \ \mathrm{S}$$

by analytic functions of variables determining the *general state* of the body.

3. Phases

It is open to us, however, to look upon any body in a heterogeneous state as an assemblage of bodies in homogeneous states. In this view, the energy, volume, and entropy of the body will be considered to be determined by the energies, volumes, and entropies of the several homogeneous portions of which the body is composed.

Some of the realizable thermodynamic states of any given

body are homogeneous states, other are heterogeneous states. In a heterogeneous state the body may consist of separate portions constituting separate bodies, as when the portions are a mass of alcohol and a glass vessel containing it. Or the body may consist of coexistent portions in different states of aggregation, as when the portions are a mass of solid salt and an overlying layer of saturated brine. In the latter case, a change of state of the body will in general involve transfers of masses from some of the constituent homogeneous portions to others. Such coexistent states of aggregation are termed **phases**. A phase shall always be understood to be physically and chemically homogeneous. It may be a solid, a liquid, or a vapor; and it may be composed of any number of independent component substances. A body consisting of r coexistent phases is said to be in an 'r-phase state'; when $r = 1$ the body is in a 'one-phase state.'

Under the general assumption here made, that the bodies under consideration are subject to no force other than a uniform and normally directed pressure, it is assumed that the influence of gravity on the thermodynamic state of a phase may be neglected. It shall be assumed also that in every solid phase the pressure is the same in every direction. And it shall be assumed that "The variations of the parts of the energy and entropy which depend upon the surfaces separating heterogeneous masses are so small in comparison with the variations of the parts of the energy and entropy which depend upon the quantities of these masses, that the former may be neglected by the side of the latter; in other words, we will exclude the considerations which belong to the theory of capillarity.*" It will be found that the influence of gravity, of states of strain in solids, of capillary tension, and of electrical actions, can best be treated in separate discussions.

When an n-component body is in a definite r-phase state, it is an assemblage of r bodies — the phases. Each of these bodies has a definite energy and a definite entropy. And since these bodies can be brought together, without change of energy or entropy, to form the n-component body, the energy and the entropy of the n-component body in its definite state are the sums of the energies and the entropies of the constituent phases. But the thermodynamic state of an n-component body can be continuously varied in a region of r-phase states; $i.\ e.,$

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* Gibbs. Scientific Papers. I., 62.

it can be varied without the disappearance of any phase or the formation of a new phase ; and when the body is brought from one state to another in the region of r-phase states the mass of each phase in general varies, and the composition of the phase may vary. In other words, none of the phases is a 'body.' In each new state of the n-component body the energy and the entropy of the body are the sums of the energies and the entropies of its phases.. Now, how do the energy and the entropy of a phase of variable component-masses vary when the phase changes from one state to another? From the definite concepts of the energy and the entropy of a *body*, we require to establish the concepts of the energy and the entropy of a *phase*.

4. The energy of a phase

Let a phase composed of any n independent components be given in any realizable quiescent state. The energy of the given phase is determined by the quantities of work and heat that are absorbed in any process of forming the phase from its components when these are taken in the 'states of reference' from which their individual energies and entropies are reckoned. In like manner, the entropy of the given phase is the limit

$$S\,\frac{dQ}{\vartheta},$$

where the indicated summation is taken over any reversible path on which the process of formation can be conducted or can be supposed to be conducted. The energy and the entropy of the phase, as thus defined, are uniquely and continuously determined by the state of the phase. The volume of the phase being likewise uniquely and continuously determinate, it appears that the energy, the volume, and the entropy of any given phase can be represented by uniform analytic functions of any independent measurable physical variables that suffice to determine the state of the phase. Such variables are the uniform temperature ϑ of the phase, the uniform pressure p that it supports, and the masses

$$M_1, M_2, \cdots M_n$$

of its independent components.

A change of the energy of a phase is obviously connected with the quantities of work and heat directly added to the

phase, and with the concurrent variation of the masses of the independent components of the phase. The general nature of this connection may be examined in the following way. Let the definite independent component-masses that constitute a phase in *any* one of its realizable states be separately given in a 'state of reference,' in which state each separate mass supports an assigned pressure p_r at an assigned temperature ϑ_r. In this state of reference, the energy of unit mass of any one of the components has an assigned value, which is zero or a constant. Let the given separate masses now be conjoined, and the resulting body be allowed to pass to some definite state, which may or may not be a homogeneous state, under the pressure p_r at the temperature ϑ_r. In this process the energy and entropy of the body change by a definite amount, and so acquire values that are wholly determined by the given masses of the n independent components.*

By reversible compression or expansion and heating or cooling, the body can be brought from its new state to every realizable state in which it is homogeneous, *i. e.*, to every realizable state of the *phase* that can be formed from the given component-masses. In any such operation, the change of the energy of the body is determined by the concurrent changes of its volume and entropy. For, without changing the volume (by compressing or expanding) or the entropy (by heating or cooling), the state cannot be changed; wherefore a given change of state, and therefore the concurrent change of energy, is determined by the concurrent change of volume and entropy. It follows that the energy of the phase is determined by the phase's volume and entropy, together with the masses of its independent components. The energy being continuously and uniformly determined, we reach the conclusion that the energy of a phase consisting of variable masses of n independent component substances can be expressed by a uniform analytic function of the volume, the entropy, and the component-masses of the phase. The energy E_i of the i-th phase of a given body is a uniform analytic function,†

$$E_i(V_i, S_i, M_{i1}, M_{i2}, \cdots M_{in});$$

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* The argument is this: The continuous ensemble of the *bodies* that constitute the phase in all its states can be brought from the states of reference (p_r, ϑ_r) of the components into a definite continuous ensemble of *states* at p_r, ϑ_r; in which *ensemble of states* the energy, the volume, and the entropy of the *ensemble of bodies* are determined by the component-masses.

† See Appendix.

where the subscript i distinguishes the phase, and the quantities V_i, S_i may be considered to be uniform analytic functions of the independent variables,

$$p, \ \vartheta, \ M_{i1}, \ M_{i2}, \ \cdots M_{in}.$$

5. Homogeneity

Consider a homogeneous body in a quiescent state and having the volume V_i, the entropy S_i, and the component-masses M_{i1}, M_{i2}, $\cdots M_{in}$. The energy of an assemblage of t such masses, when t is any real number, will be

$$t \cdot E_i(V_i, \ S_i, \ M_{i1}, \ M_{i2}, \ \cdots M_{in}).$$

If the t masses are conjoined, a homogeneous mass will be formed without change of the total volume or the total entropy of the masses. So the energy of the new mass will be

$$E_i(tV_i, \ tS_i, \ tM_{i1}, \ tM_{i2}, \ \cdots tM_{in}).$$

No work or heat having been absorbed in this process, the energy of the resulting total mass is equal to the total energy of the originally given separate masses,

$$E_i(tV_i, tS_i, tM_{i1}, tM_{i2}, \cdots tM_{in}) = t \cdot E_i(V_i, S_i, M_{i1}, M_{i2}, \cdots M_{in}).$$

In other words, a t-fold change of the volume, entropy, and component-masses of a phase effects a t-fold change of the energy of the phase; the *uniform analytic* function E_i of the variables

$$V_i, \ S_i, \ M_{i1}, \ M_{i2}, \ \cdots M_{in}$$

is a *homogeneous* function of the *first degree* in these variables.

6. The energy of a body

Since the energy of a body in any state of a given region of r-phase states is equal to the sum of the energies of the r constituent phases, this energy can be given the *analytical* expression

$$E = E_1 + E_2 + \cdots + E_r.$$

In this formulation the energy of the body, with reference to the given region of states, is expressed as a function of the volumes, the entropies, and the component-masses of the con-

stituent phases.   The relation is subject to the n equations of condition,

$$M_{1j} + M_{2j} + \cdots + M_{nj} = M_j, \quad (j = 1, 2, \cdots n)$$

which expresses that E is the energy of the *body* composed of the constant masses

$$M_1, M_2, \cdots M_n$$

of the n independent components.

With reference to the given region of states, the volume V and the entropy S of the body are expressed by the relations

$$V = V_1 + V_2 + \cdots + V_r,$$

$$S = S_1 + S_2 + \cdots + S_r.$$

7. The differential of the phase-energy

For any constant values of the component-masses, the differential of the phase-energy

$$E_i(V_i, \ S_i, \ M_{i1}, \ M_{i2}, \ \cdots \ M_{in})$$

is

$$dE_i = \frac{\partial E_i}{\partial V_i}\, dV_i + \frac{\partial E_i}{\partial S_i}\, dS_i.$$

Now, by the two laws of thermodynamics, the differential of the energy of the body composed of these constant component-masses is

$$dE_i = -\, pdV_i + \vartheta dS_i,$$

where p, ϑ are the pressure and temperature of the body.   The first of these equations can be identical with the second, for all constant values of the component-masses, only if it is generally true that

$$\frac{\partial E_i}{\partial V_i} = -\, p, \qquad \frac{\partial E_i}{\partial S_i} = +\, \vartheta.$$

If, then, we write

$$\mu_{ij} = \frac{\partial E_i}{\partial M_{ij}}$$

for the derivative of the energy of the phase with regard to the mass of the j-th component, the differential of the energy of the phase is

$$dE_i = -\, pdV_i + \vartheta dS_i + \mu_{i1}dM_{i1} + \mu_{i2}dM_{i2} + \cdots + \mu_{in}dM_{in}.$$

The function μ_{ij} is termed the **potential** of the j-th component in the i-th phase of the body.

The energy of a phase composed of the variable mass M_i of a single component is a homogeneous, uniform, analytic function of the first degree,

$$\mathrm{E}_i = \mathrm{E}_i\,(\mathrm{V}_i,\ \mathrm{S}_i,\ \mathrm{M}_i)\,;$$

and the differential of this phase-energy is

$$d\mathrm{E}_i = -\,pd\mathrm{V}_i + \vartheta d\mathrm{S}_i + \mu_i d\mathrm{M}_i.$$

By Euler's theorem of homogeneous functions, the functions

$$\mathrm{E}_i,\quad \mathrm{V}_i,\quad \mathrm{S}_i,\quad \mu_i,$$

and the variables

$$p,\quad \vartheta,\quad \mathrm{M}_i,$$

satisfy the relation

$$\mathrm{E}_i = -\,p\mathrm{V}_i + \vartheta \mathrm{S}_i + \mu_i \mathrm{M}_i.$$

In the independent variables p, ϑ, M_i, the differential of the phase-energy is

$$d\mathrm{E}_i = \left(-\,p\,\frac{\partial \mathrm{V}_i}{\partial p} + \vartheta\,\frac{\partial \mathrm{S}_i}{\partial p}\right) dp$$

$$+ \left(-\,p\,\frac{\partial \mathrm{V}_i}{\partial \vartheta} + \vartheta\,\frac{\partial \mathrm{S}_i}{\partial \vartheta}\right) d\vartheta$$

$$+ \left(-\,p\,\frac{\partial \mathrm{V}_i}{\partial \mathrm{M}_i} + \vartheta\,\frac{\partial \mathrm{S}_i}{\partial \mathrm{M}_i} + \mu_i\right) d\mathrm{M}_i.$$

8. Summary of Chapter II.

The application of the energy and entropy laws to the thermodynamic behavior of a body subject to no force other than a uniform and normally directed pressure is expressed by the relation,

$$d\mathrm{E} = -\,pd\mathrm{V} + \vartheta d\mathrm{S},$$

between quantities $\mathrm{E}, p, \mathrm{V}, \vartheta, \mathrm{S}$ that are determined by the state of the body. It is desired to replace these *physical quantities* by uniform analytic *functions* of independent measurable physical variables that determine the state ; to the end that the relation

shall afford an *analytical theory* of the thermodynamics of the body.

Since, however, the state of the body changes discontinuously when the body passes from one continuous region of thermodynamic states to another; and since the general state of the body cannot be specified by a single set of independent variables; it seems impracticable to attempt immediate replacement of the quantities in question by analytic functions of variables determining the general thermodynamic state of the body.

It is practicable, however, to consider a body in a heterogeneous state as an assemblage of bodies in homogeneous states; and so to consider the energy, volume, and entropy of the assemblage of bodies as determined by the energies, volumes, and entropies of its homogeneous parts. But the heterogeneous body may be an assemblage of *phases*, which are not *bodies*. Yet the energy, volume, and entropy of such a body remain the sums of the energies, volumes, and entropies of its phases; and these latter quantities are determinate.

For the energy and entropy of a phase are determined by the quantities of work and heat absorbed in the formation of the phase from its components when these are taken in the states of reference from which their individual energies and entropies are reckoned. Thus defined, the energy and entropy of the phase are uniquely and continuously determined by the state of the phase, and so can be replaced by uniform analytic functions of the pressure, temperature, and component-masses of the phase. Further, the continuous ensemble of the bodies that constitute the phase in all its states can be brought from the states of reference (p_r, ϑ_r) of the components into a continuous ensemble of states at p_r, ϑ_r, in which ensemble of states the energy, volume, and entropy of the ensemble of bodies are determined by the component-masses. The change of the energy of any body of the ensemble of bodies, when the body is then brought to any homogeneous state, is determined by the concurrent change of the volume and entropy of the body. Consequently, the general energy of the phase is uniquely and continuously determined by the volume, the entropy, and the independent component-masses of the phase; and so can be expressed by a uniform analytic function of these variables. And since a phase with t-fold volume, entropy, and component-masses has t-fold energy, this uniform analytic function is homogeneous and of the first degree.

On differentiating the energy,

$$E_i(V_i, S_i, M_{i1}, M_{i2}, \cdots M_{in}),$$

of the i-th phase of a body in an r-phase state, and comparing with the relation

$$dE_i = -pdV_i + \vartheta dS_i,$$

which must be satisfied when the component-masses have any constant values, it appears that the differential of the energy of the phase is,

$$dE_i = -pdV_i + \vartheta dS_i + \sum_{j=1}^{j=n} \frac{\partial E_i}{\partial M_{ij}} dM_{ij}.$$

In the case of a one-component phase,

$$E_i = E_i(V_i, S_i, M_i),$$

$$dE_i = -pdV_i + \vartheta dS_i + \mu_i dM_i;$$

and the quanities E_i, V_i, S_i, μ_i may be considered to be functions of the independent variables p, ϑ, M_i.

APPENDIX

The Energy of a Phase

The reasoning employed in the text (p. 106), to establish that the energy of a phase is an analytic function of the volume, entropy, and component-masses of the phase, is perhaps made more clear by comparison with the summary statement given on p. 110. The end may be sought in another way, through consideration of the elimination of p,ϑ between the three given equations,

$$E = E(p,\vartheta,M\text{'s})$$
$$V = V(p,\vartheta,M\text{'s})$$
$$S = S(p,\vartheta,M\text{'s}) ;$$

whose second members are uniform analytic functions of the variables.

Let it be supposed that the equations

$$V - V(p,\vartheta,M\text{'s}) = 0$$
$$S - S(p,\vartheta,M\text{'s}) = 0$$

are satisfied by the particular values

$$p_1, \quad \vartheta_1, \quad M_1\text{'s}, \quad V_1, \quad S_1 ;$$

and that the first members of these equations are continuous functions of the arguments for values in the neighborhood of the system just given. Since, now, the derivatives,

$$\frac{\partial V}{\partial p}, \quad \frac{\partial V}{\partial \vartheta}, \quad \frac{\partial S}{\partial p}, \quad \frac{\partial S}{\partial \vartheta},$$

exist and are continuous in the neighborhood of this system of values ; and the determinant

$$\begin{vmatrix} \dfrac{\partial V}{\partial p} & \dfrac{\partial V}{\partial \vartheta} \\[2ex] \dfrac{\partial S}{\partial p} & \dfrac{\partial S}{\partial \vartheta} \end{vmatrix}$$

does not vanish for this system of values (*i. e.*, V,S are independent functions) ; we have

$$p = \phi_1(V,S,M\text{'s})$$
$$\vartheta = \phi_2(V,S,M\text{'s}) ;$$

which values of p,ϑ satisfy the original equations, and reduce to p_1,ϑ_1 when V,S,M's become V_1,S_1,M_1's. Moreover, ϕ_1,ϕ_2 possess partial derivatives of the first order (Goursat, Mathematical Analysis, Hedricks translation, p. 145).
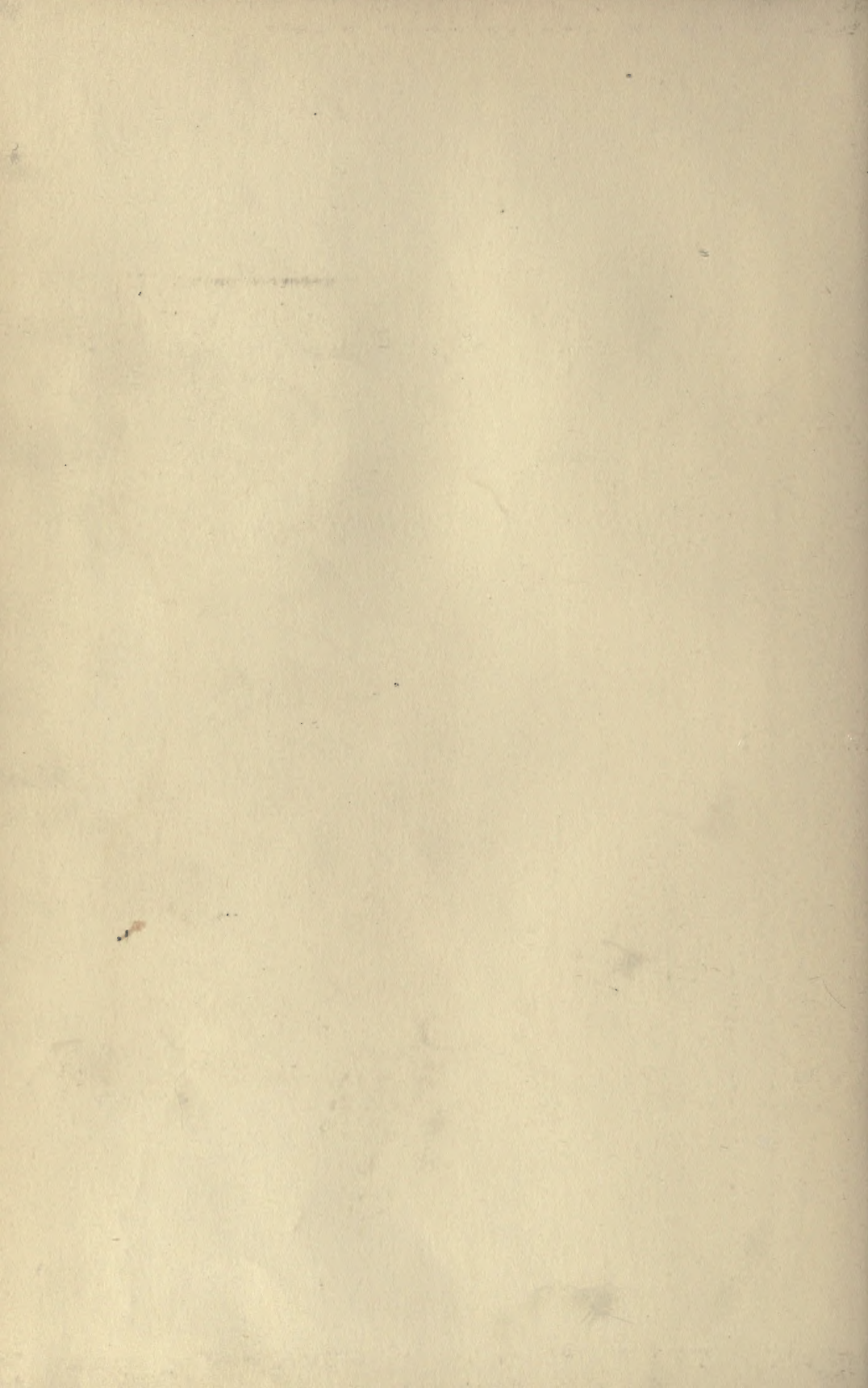
So we have

$$E = E\big(\phi_1(V,S,M\text{'s}),\phi_2(V,S,M\text{'s}),M\text{'s}\big)$$
$$= E_1(V,S,M\text{'s}) ;$$

and E_1 is a continuous function of its arguments. Accordingly, the function E_1 can be expressed, with any desired accuracy, by an analytic function of V,S,M's.